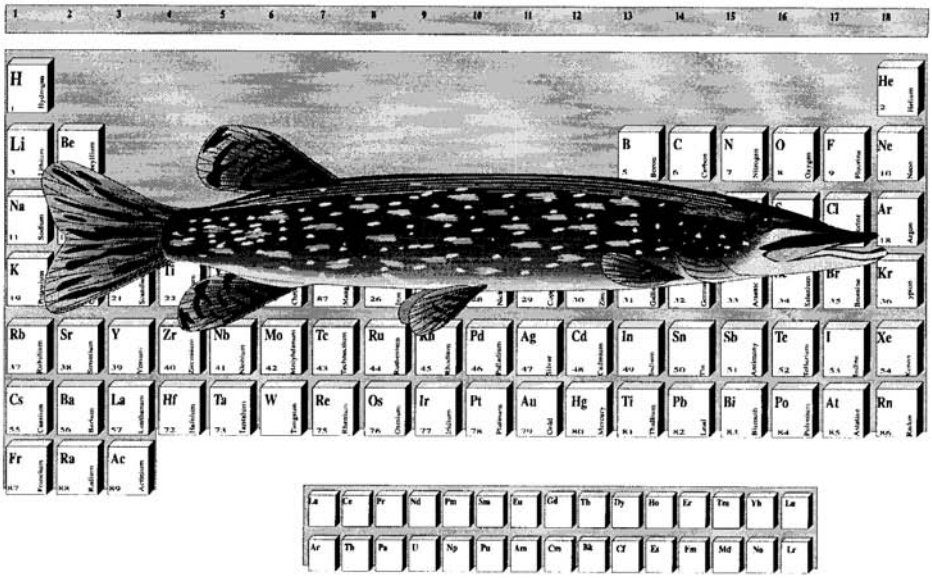
NAES-TR-96-03
Study #7-7105-1261

TECHNICAL REPORT

# WATER QUALITY AND METAL AND METALLOID CONTAMINANTS IN SEDIMENTS AND FISH OF KOYUKUK, NOWITNA, AND THE NORTHERN UNIT OF INNOKO NATIONAL WILDLIFE REFUGES, ALASKA, 1991



by

**Keith A. Mueller**
**Elaine Snyder-Conn**
**Mark Bertram**

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

**December 3, 1996**

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# WATER QUALITY AND METAL AND METALLOID CONTAMINANTS IN SEDIMENTS, AND FISH OF KOYUKUK, NOWITNA, AND THE NORTHERN UNIT OF INNOKO NATIONAL WILDLIFE REFUGES, ALASKA, 1991

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## EXECUTIVE SUMMARY

This study was conducted by U.S. Fish and Wildlife Service biologists during 1991. The study goals were to monitor water quality and concentrations of metals and metalloids in stream sediments and fish, and to evaluate existing and potential impacts of metal contamination and water quality degradation on refuge fish and wildlife. Stream sediment, water, and fish samples were collected from 12 sites: four sites on Northern Innoko National Wildlife Refuge, two south of the Northern Innoko National Wildlife Refuge, two north of the Koyukuk National Wildlife Refuge, and four on the Nowitna National Wildlife Refuge.

Mineral deposits of many types have been located around the three refuges. These include antimony, arsenic, bismuth, copper, lead, gold, molybdenum, nickel, silver, tin, thorium, tungsten, uranium, and zinc. Extraction of these resources could affect fish and wildlife resources of the refuges, downstream of these deposits. Placer mining for gold has occurred in many of the major and minor drainages that enter the refuges.

Streams sampled had soft water and were calcium and magnesium bicarbonate-dominated. Hardness values were extremely low at Clear Creek and the Hogatza River, and high at the Sulukna River and Sulukna Adjacent Pond. Hardness values at other sites were moderate. All pH values were 7.0 - 7.3 except the Sulukna River and Sulukna Adjacent pond which were 8.3 and 7.6, respectively. Alkalinity values closely corresponded to hardness values. Sulfates, if present, were present in low concentrations. Sulukna Adjacent pond had high values of conductivity, hardness, and alkalinity likely due to evaporative concentration. Clear Creek was slightly turbid due to bank erosion, while the Hogatza River was turbid due to bank erosion and placer mining activity upstream of the sample site.

In general, concentrations of beryllium, cadmium, lead, and mercury in sediment samples were characteristic of uncontaminated sediments. Mercury concentrations in sediment were all <0.14 mg/kg. Mean concentrations of cadmium and lead in sediment samples were greatest on Koyukuk Refuge, and mean concentrations of copper, manganese, nickel, and zinc were greatest on Northern Innoko Refuge. Concentrations of beryllium, cadmium, copper, lead, manganese, and nickel were lowest in sediment samples from the Nowitna Refuge.

Several investigators list copper concentrations <20-25 mg/kg as background conditions for sediment. Copper concentrations exceeded 25 mg/kg at all Northern Innoko and Koyukuk refuge sites, and at two of four sites on Nowitna Refuge. Concentrations of nickel <20-31 mg/kg have been reported as background conditions. Nickel concentrations exceeded 31 mg/kg at all sites, except Sulukna River and Sulukna Adjacent pond, which exceeded 28 mg/kg. Reported background concentration estimates of zinc range from 50 mg/kg to 100 mg/kg; the mean zinc concentration for all sites was 91 mg/kg.

Mean concentrations of beryllium, boron, cadmium, copper, lead, manganese, nickel, and strontium in sediment were not significantly different above and below the Camp Creek mine. Zinc concentrations were significantly greater above the mine than below. In general, samples from mined streams did not have higher concentrations of metals in sediments than those from unmined streams. Although greater than in other studies, copper and zinc concentrations from our study seem to be within the normal range for Northern Innoko, Nowitna, and Koyukuk refuges.

Arctic grayling, northern pike, and sheefish are highly migratory species and, thus, assigning the origin of contaminants found in these species is difficult, if not impossible. Cadmium, iron, magnesium, manganese, mercury, selenium, and zinc accumulated differentially in tissues of northern pike and sheefish. The pattern of accumulation for cadmium, magnesium, selenium, and zinc in northern pike was kidney>liver>muscle. In northern pike, kidney and muscle concentrations of mercury were significantly greater than in liver.

Arsenic, cadmium, and zinc concentrations in tissue were low. Mercury was detected in each fish regardless of location, except for the one Alaska blackfish collected. Mean concentrations of mercury in muscle samples were from 3.3 to 8.6 times greater than the mean background concentrations reported by other investigators. Eight northern pike and four sheefish had at least one tissue with mercury concentrations greater than 4.0 mg/kg, the approximate dry weight equivalent of the Food and Drug Administration 1.00 mg/kg wet weight action concentration for mercury. Selenium has been shown to strongly bind with methylmercury, a highly bioavailable and toxic form of mercury, providing an antagonistic effect. Selenium concentrations exceeded mercury concentrations in all kidney and liver samples of northern pike; however, mercury concentrations exceeded selenium concentrations in all northern pike muscle samples.

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## ACKNOWLEDGMENTS

The authors thank the staff of Koyukuk, Nowitna, and Northern Unit of the Innoko National Wildlife Refuges for their assistance during the field portion of this study. We also thank Everett Robinson-Wilson, Fish and Wildlife Service, Region 7; Patrick Sousa, Ecological Services Fairbanks, Supervisor; Phyllis Scannell Weber, Alaska Department of Fish and Game, Habitat Division; Tom Eley, Refuge Manager, Koyukuk, Nowitna, and Northern Unit of the Innoko National Wildlife refuges and his staff; and Ken Russell, Fish and Wildlife Service, Fairbanks Fisheries Office, who carefully reviewed drafts of this document. Their efforts are greatly appreciated and added significantly to the quality of this document. Barbara Boyle, Fish and Wildlife Service, Ecological Services Fairbanks, created most of the figures for this report.

# INTRODUCTION

The Koyukuk National Wildlife Refuge, the Northern Unit of the Innoko National Wildlife Refuge (Northern Innoko Refuge), and the Nowitna National Wildlife Refuge, located in westcentral Alaska, were created by the Alaska National Interest Lands Conservation Act of 1980 (ANILCA). Among the purposes of the refuges, as prescribed in ANILCA, are the conservation of fish and wildlife populations and habitats in their natural diversity, and ensuring water quality and quantity, to the maximum extent practicable, within the refuges (U.S. Fish and Wildlife Service 1987a,b).

To meet these goals, ANILCA mandates identification and description of problems which may adversely affect fishery resources and wildlife populations. This study is a continuation of the effort to fulfill aspects of that obligation by examining water quality and baseline concentrations of metals in aquatic ecosystems and potential on-refuge effects from placer mining occurring upstream of the refuges.

Refuge fish, wildlife and habitat resources, geology and mineral occurrences, and mining history of refuge areas were reviewed by Snyder-Conn et al. (1992a) and Snyder-Conn et al. (1992b). Briefly, the three refuges are primarily comprised of wetland and lowland areas. The Koyukuk Refuge is approximately 1.5 million hectares (3.6 million acres) in size and contains Koyukuk Flats which ranges from 8 to 32 km (5-20 mi) in width. The Koyukuk River divides the refuge flowing from the northeast to the southwest. The Northern Innoko Refuge, also known as Kaiyuh Flats, is approximately 145,000 hectares (351,000 acres) in size. The Nowitna Refuge is 830,655-hectare (2,051,000 acres) in size and is bisected into eastern and western sections by the Nowitna River and adjacent wetlands. The abundant wetlands and forested floodplains of the refuges offer prime habitat for aquatic life, waterfowl and other birds, including the endangered American peregrine falcon (*Falco peregrinus anatum*).

Sites of known or indicated mineralization in and near the Koyukuk and Northern Innoko refuges (Cobb 1970a,b, 1972, 1974, 1975a,b, 1984a,b,c,d,e, 1985; Eberlein et al. 1977; Cruz and Cobb 1984a, 1986; U.S. Bureau of Mines 1987; Alaska Division of Geological and Geophysical Surveys 1991) are identified in Figure 1. Gold, in lode sources and placer deposits, has been the dominant mineral mined in areas surrounding the refuges. Few stream placer or mineable metal deposits have been located within the refuges. Areas surrounding the Koyukuk Refuge contain enriched deposits of antimony, bismuth, chromium, copper, iron, lead, manganese, molybdenum, nickel, platinum-group metals, silver, thorium, tungsten, uranium, and zinc (Berg and Cobb 1967; Cobb 1972; Clark et al. 1974; Cobb 1975a,b, 1984b,c,d; Cruz and Cobb 1986; Alaska Division of Geological and Geophysical Surveys 1991; Shirley Liss, Alaska Division of Geological and Geophysical Surveys, Fairbanks, pers. comm.). No mercury deposits have been documented within

areas covered by the five USGS quadrangle maps which include the refuges (Shungnak, Hughes, Kateel River, Melozitna, and Nulato) (Bottge 1986).

The Northern Innoko Refuge is bordered on the east by the Kaiyuh Mountains, which are part of a geologic province characterized by deposits of antimony, copper, gold, lead, tin, tungsten, and zinc, with secondary deposits of antimony, copper, and silver (Holzheimer 1926; Clark et al. 1974; Nokleberg et al.1987).

Many deposits of minerals occur within the Nowitna River drainage (Cobb 1970a,b, 1974a, 1975a, 1984a,b,c,d, 1985, Eberlein et al. 1977, Cruz and Cobb 1984, 1986, U.S. Bureau of Mines 1987) (Figure 2). These include antimony, bismuth (Cobb 1970a), copper (Cobb 1984b), extensive placer gold deposits, lode gold (Cobb 1984e), lead (Thomas 1964, Cobb 1984a), mercury (Cruz and Cobb 1984a, 1986), tin-tantalum-niobium (Cruz and Cobb 1984b, Warner 1985), platinum (Cobb 1975b), tungsten (Cobb 1985), and uranium (Cobb 1970b). 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). Among the important minerals present in the highly mineralized Kuskokwim Mountains are antimony, arsenic, bismuth, copper, gold, lead, mercury, molybdenum, silver, tin, tungsten, and zinc (Malone 1962, Patton et al. 1982, King et al. 1983, Patton and Moll 1983).

Preliminary sampling for water quality and metals concentrations in water occurred during 1986 at the Koyukuk and Northern Innoko refuges (Snyder-Conn 1992a), and during 1985 at the Nowitna Refuge (Snyder-Conn 1992b). Study objectives were established and sampling was expanded during 1987 and 1988 on all three refuges to include determinations of water quality variables and metals concentrations in water, sediment, and fish tissue.

Water quality at all three refuges was similar: slightly basic or near neutral pH, and soft to moderate hardness and alkalinity, indicative of a well-buffered calcium/magnesium bicarbonate watershed (Snyder-Conn 1992a,b). The Sulatna River, an actively mined stream, had anomalously high turbidity levels. Most trace element concentrations in water and sediment were within the range expected for uncontaminated watersheds. At some sites, aluminum, iron, manganese, nickel, and vanadium in water had greater concentrations than is normally found in unimpacted waters; however, none of the metals concentrations were expected to greatly impact aquatic resources (Snyder-Conn et al. 1992a,b). Snyder-Conn et al. (1992a) identified high concentrations of mercury in northern pike (*Esox lucius*) within the Koyukuk River drainage, but the mercury data were of questionable quality due to poor Quality Assurance/Quality Control (QA/QC). On the Nowitna Refuge, Snyder-Conn et al. (1992b) identified high concentrations of mercury in northern pike liver, kidney, and muscle. Our investigation is a follow-up to these previous studies.

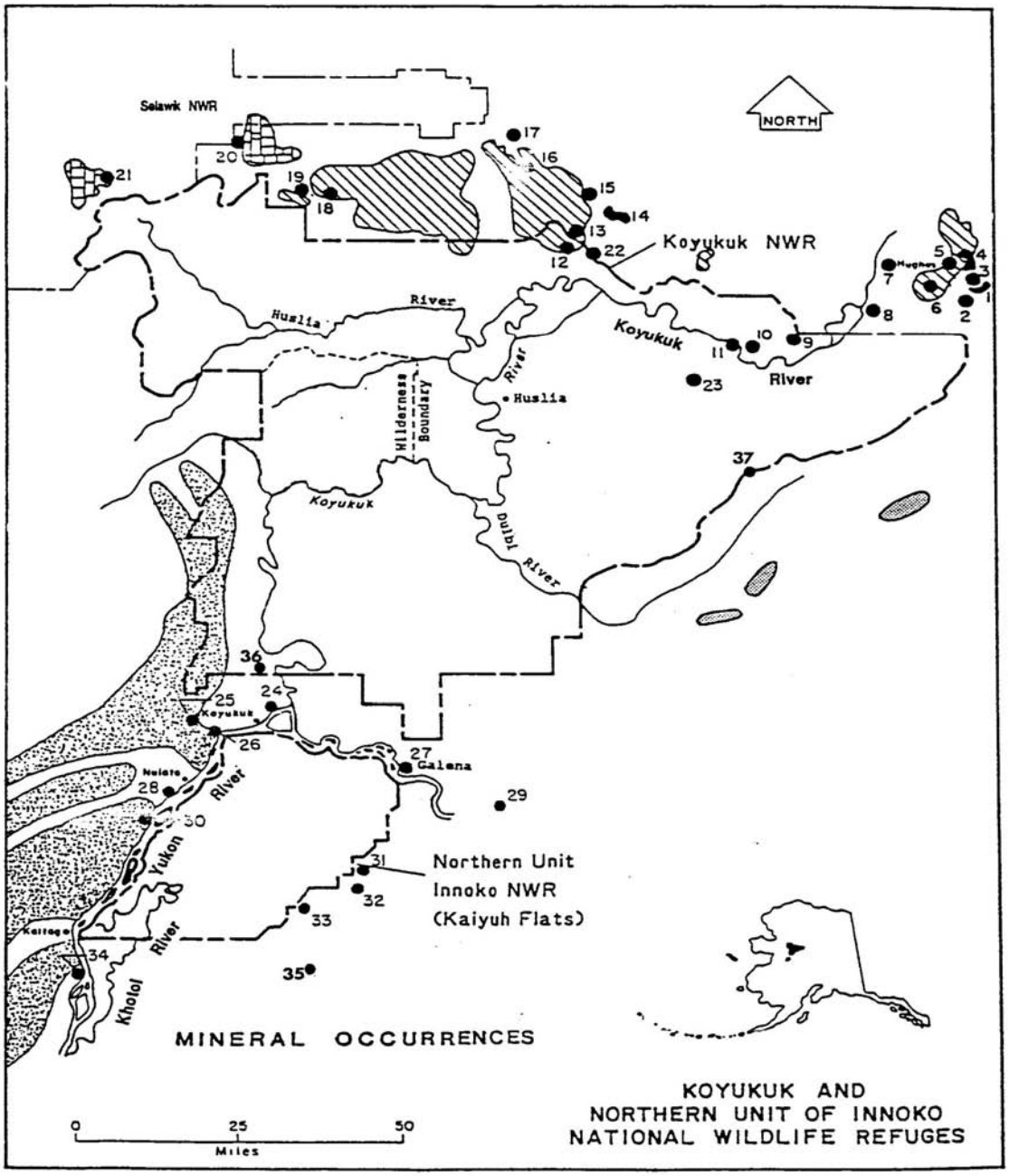


Figure 1. Regional mineral occurrences near Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge.

## Legend - Mineral Occurrences

Produced placers, prospects, visible ore minerals, favorable geology, geochemical anomalies, and other indications of mineralization. Elements in parentheses are present in anomalous amounts in sediments and rock chips.

1. Utopia Creek placer (Au)
2. South of Utopia Creek - intrusives along fault zone in andesite and barite boulders (Ag, Pb, Zn, Cu, Sb, Au)
3. North of Utopia Creek - intrusives and alteration in andesite; visible ore minerals (Pb, Zn Cu, Mo, Ag, Au)
4. Indian River and Black, Felix, and Snyder creek placers (Au)
5. Black Creek Area - altered volcaniclastics near pluton contact (Cu)
6. Pocahontas Creek placer (Au)
7. Hughes Bar placer (Au)
8. Florence Bar placer (Au)
9. Sun Mountain area - dikes, limestone, altered andesite
10. Sun Mountain prospect (Cu?)
11. Batza Slough-large float block high in Ag, Pb, Au
12. Unnamed prospect - intrusive and veins in and near border phase of pluton (Ag, Au, Pb, Bi, W, Cu)
13. Caribou Mt.- quartz monzonite with disseminate U, Th-bearing minerals
14. Bear Creek (Hogatza) placer (Au, Cu)
15. Pluton east of Zane Hills - bostonite and nepheline syenite dikes (U)
16. South Dakli area - gently dipping pluton contact, probable roof zone, quartz veins, visible ore minerals (Cu)
17. North Dakli area - 3-ft-thick quartz veins in altered andesite, probable roof zone (Cu)
18. West end Wheeler Creek pluton - uraniferous alaskite (U, Th)
19. Upper Billy Hawk Creek area - 10 $mi^2$ area of 1-2 ft thick quartz veins, visible ore minerals (Ag, Pb, Cu)
20. Shovel Creek placer area-pluton contact, probable quartz-tourmaline sulphide veins (Au)
21. Ekiek pluton contact zone (U, Th)
22, 23. Lode claims. No longer valid claims in BLM records
24. Koyukuk Island (Bituminous coal prospect)
25. Nulato Coal Bed (Bituminous coal prospect)
26. Pickart Mine (Bituminous coal), past producer
27. Galena Mill (Sand and gravel), past producer
28. Busch Mine (Bituminous coal), past producer
29. Nahoclatilten (Bituminous coal), past producer
30. Blatchford Mine (Bituminous coal), past producer
31. Perseverence Mine (Pb), past producer
32. Bishop Creek headwaters (Ag), past producer
33. Camp Creek placer placer (Au)
34. Adolph Muller Prospect (Bituminous coal prospect)
35. Eddy Creek west of Round Top Mt. (Ag, Cu, Mo, Pb, An, W)
36. Forty Seven Creek (Ag, Au, Sb, Te, W)
37. Hochandochtla Mt. (Cu)

Terranes favorable or permissible for mineral deposits


**Alkalic granite**


**Undivided granite, including alkalic plutons - Au**


**Ophiolite terrane - Cr, Co, Ni, Pt**


**Coal-bearing sandstone and shale**

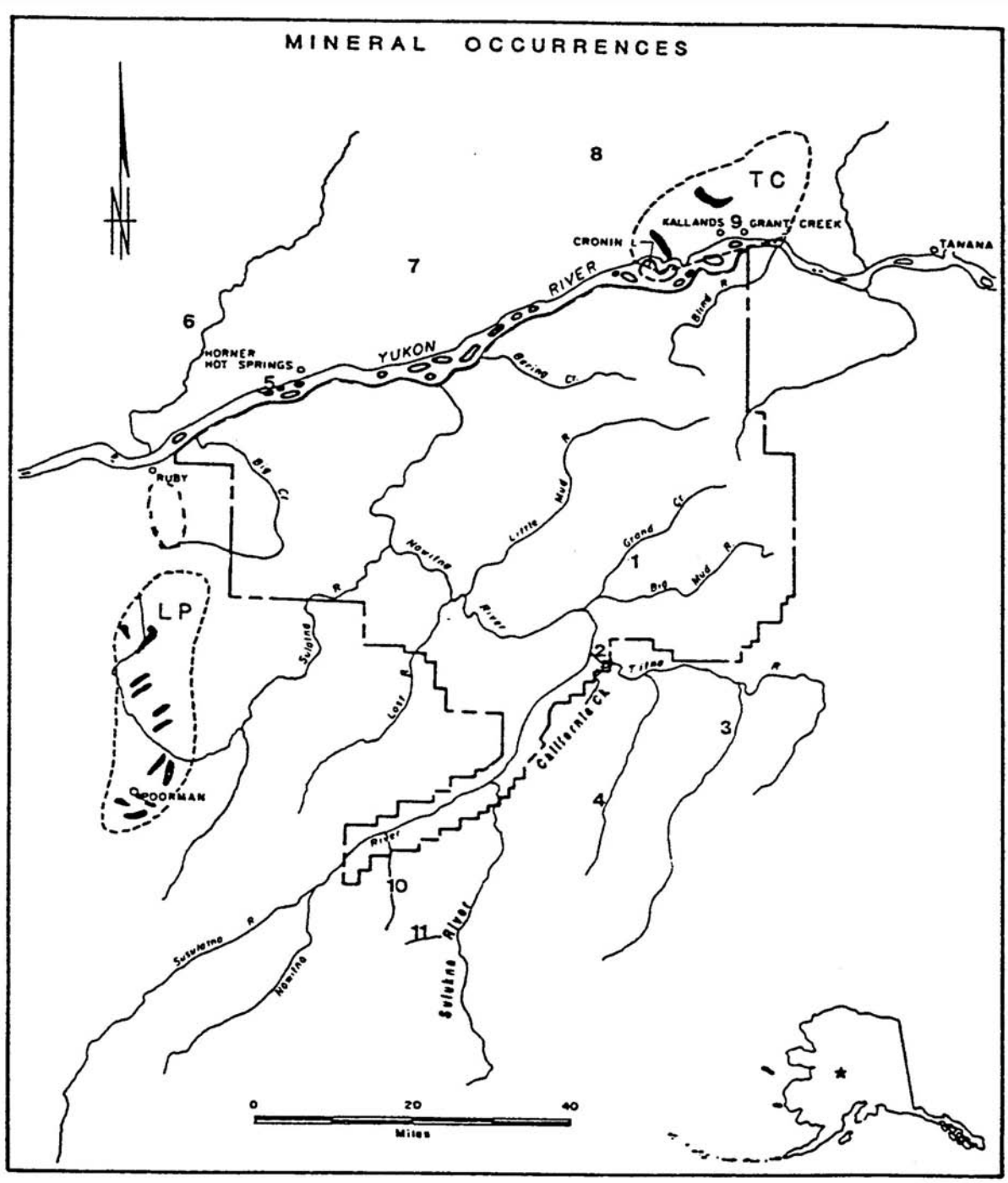


Figure 2. Regional mineral occurrences near the Nowitna National Wildlife Refuge. See text for sources.

## 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

The objectives of this study were to:

1. Quantify the distribution of elevated mercury concentrations in fish within the Koyukuk, Northern Innoko, and Nowitna refuges;

2. Compare concentrations of metals in sediments and fish tissue among watersheds where placer mining has and has not occurred;

3. Obtain additional baseline water quality and metal data on sediments and fish within these refuges;

4. Evaluate existing and potential impacts of metal contamination and water quality degradation on refuge fish and wildlife resources.

## METHODS AND MATERIALS

### *Sample Sites*

Samples were collected from 12 sites, 4 on the Northern Innoko Refuge, 2 south of the Northern Innoko Refuge, 2 north of the Koyukuk Refuge, and 4 on the Nowitna Refuge (Figures 3, 4, and 5). Sample site descriptions are as follows.

Site KY4, Clear Creek, an unmined drainage, at the confluence with the Hogatza River, T. 10 N, R. 16 E, Sec. 32, SE 1/4, Kateel River Meridian (KRM); 66°13'06" N, 155°30'00" W.

Site KY6, Hogatza River, at the mouth of Carbou Creek, a mined drainage, T. 9 S, R. 16 E, Sec. 16, NE 1/4, KRM; 66°10'59" N, 155°26'59" W.

Site IN11, a lake adjacent to Lower Camp Creek on the Northern Innoko Refuge, T. 9 N, R. 16 E, Sec. 6, KRM; 64°27'03" N, 157°40'25" W.

Site IN12, Camp Creek downstream of a placer mine, T. 13 S, R. 7 E, Sec. 8, KRM; 64°24'50" N, 157°32'45" W.

Site IN13, Camp Creek upstream of a placer mine, T. 13 S, R. 7 E, Sec. 17, KRM; 64°24'00" N, 157°32'45" W.

Site IN14, Lower Camp Creek on the Northern Innoko Refuge, T. 12 S, R. 7 E, Sec. 6, KRM; 64°28'35" N, 157°43'05" W. This site was part of the Kaiyuh Flats lake system at high water.

Site IN16, Eddy Creek, an unmined drainage, on the Northern Innoko Refuge, T. 13 S, R. 5 E, Sec. 13, KRM; 64°23'15" N, 157°47'00" W.

Site IN17, a lake adjacent to Eddy Creek on the Northern Innoko Refuge, T. 13 S, R. 5 E, Sec. 13, KRM; 64°23'30" N, 157°47'35" W.

Site NO2, Sulatna River, a mined drainage, T. 11 S, R. 21 E, Sec. 31, SE 1/4, KRM; 64°29'50" N, 154°44'00" W.

Site NO4, Sulukna River, possibly a historically mined drainage, immediately upstream of the confluence with the Nowitna River, T. 6 S, R. 25 E, Sec. 1, SW 1/4, KRM; 64°07'50" N, 154°02'46" W.

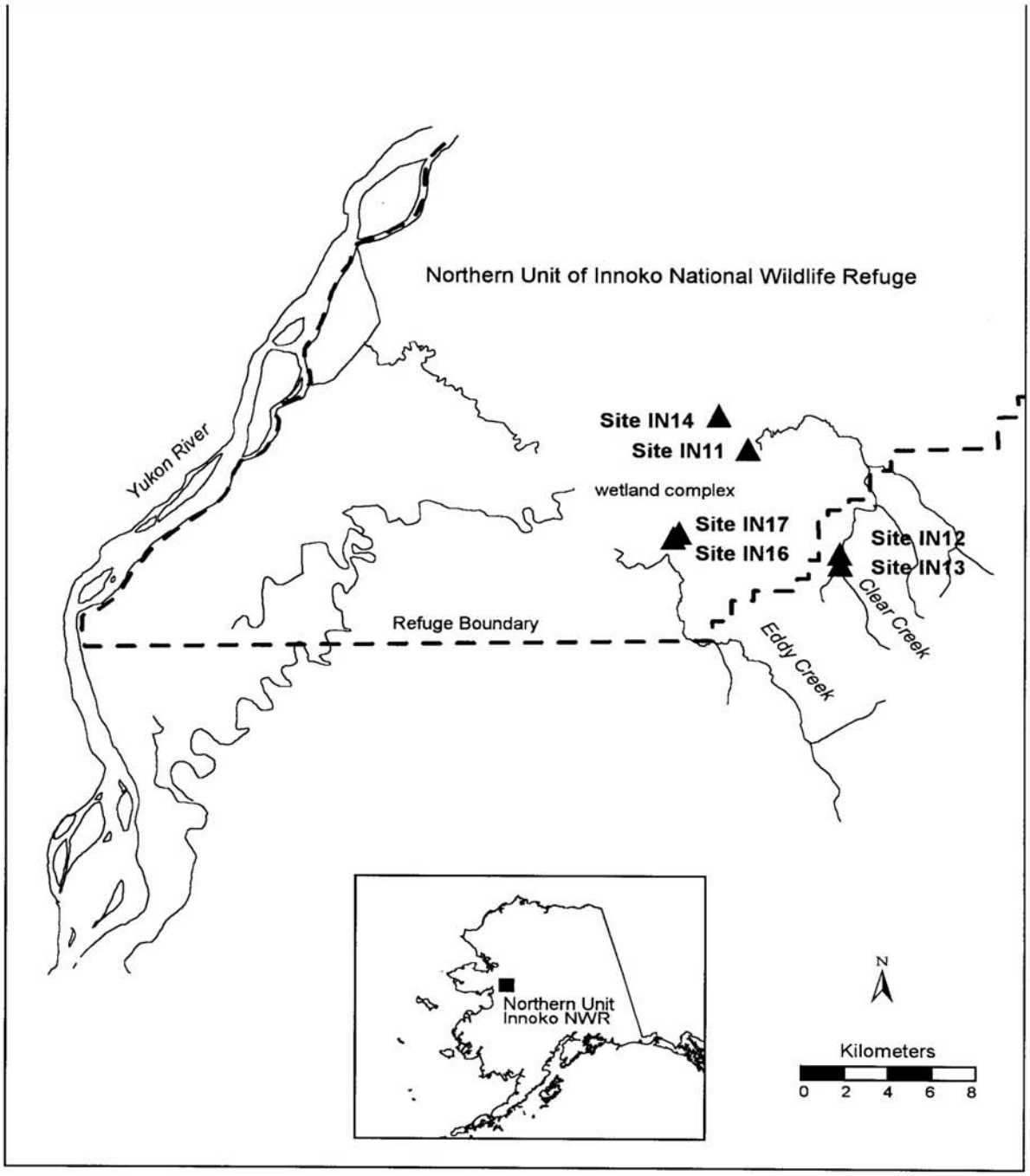


Figure 3. Location of sample sites on Koyukuk and Northern Innoko National Wildlife refuges, Alaska, 1991.

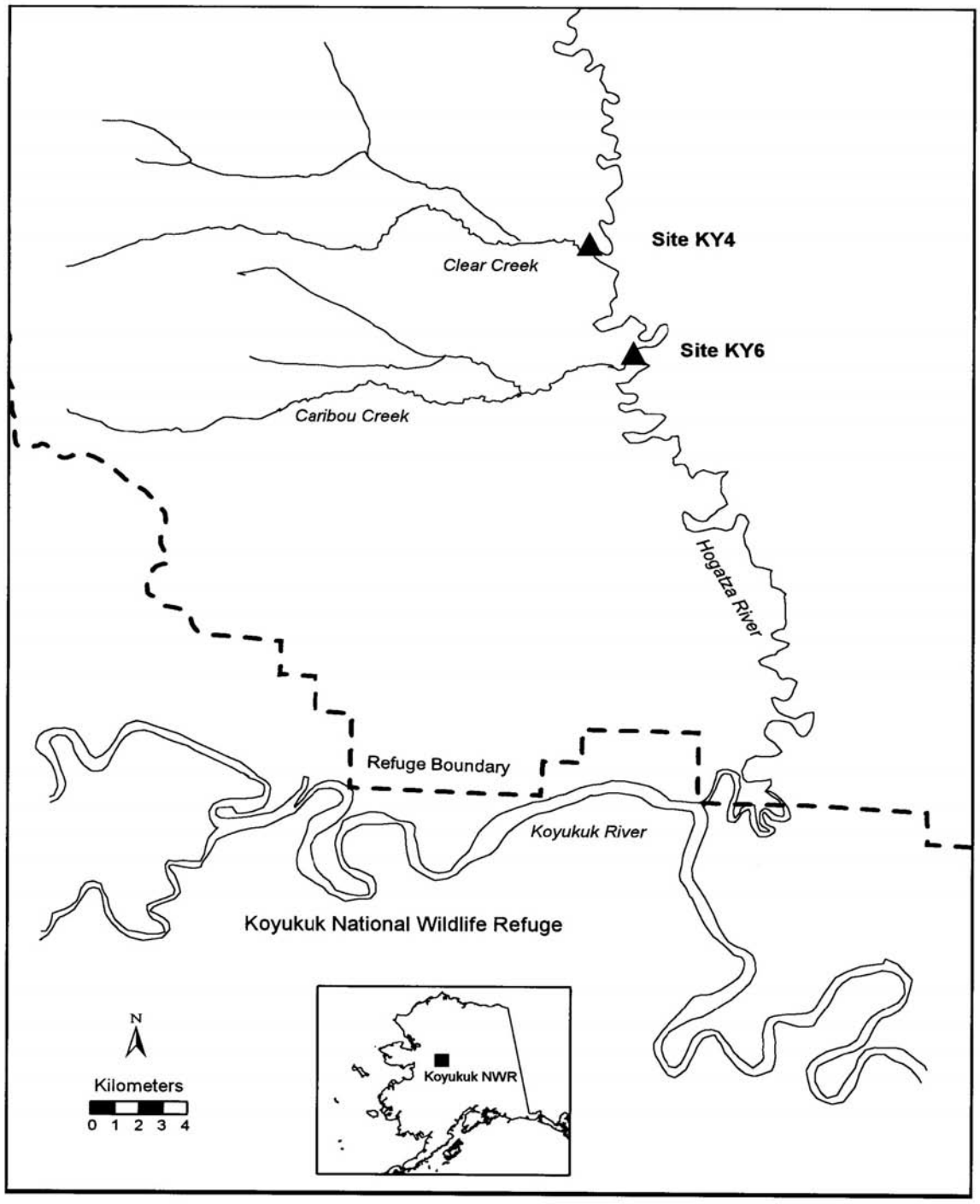


Figure 4. Location of sample sites on Koyukuk National Wildlife Refuge, Alaska, 1991.

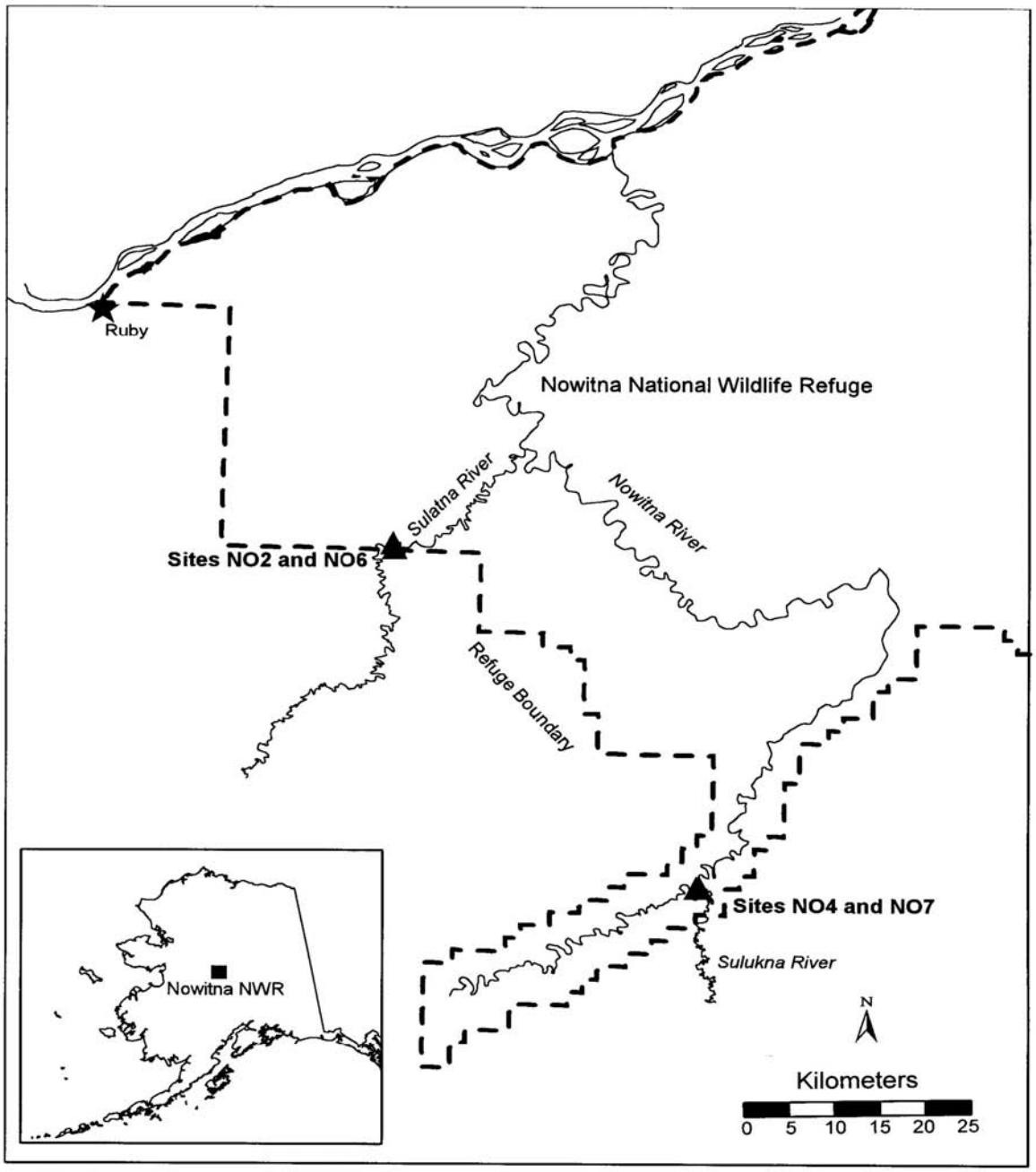


Figure 5. Location of sample sites on Nowitna National Wildlife Refuge, Alaska, 1991.

Site NO6, a lake (Cross Lake) adjacent to the Sulatna River, T. 11 S, R. 21 E, Sec. 31, SE 1/4, KRM; 64°29'28" N, 154°44'00" W.

Site NO7, a small pond immediately adjacent to the Sulukna River, T. 6 S, R. 25 E, Sec. 1, SW 1/4, KRM; 64°07'50" N, 154°02'46" W.

Sediment and fish tissue samples at these sites were collected for metals analysis. Water samples were collected for analysis of water quality variables.

*Collection Methods*

Water Quality Samples

Single 1-L water quality samples were collected between 12-19 June 1991. Water quality sample containers were triple-rinsed in the water to be sampled prior to sampling. Water samples were collected by direct surface grabs. During river sampling, each sample bottle was extended into the current upstream from the collector to avoid contamination due to resuspension of sediment or from the collector. Sample bottles were filled to the top to minimize gaseous exchange. Each sample bottle was labeled prior to collection and placed in a cooler with ice for transport to a field laboratory for analysis.

Samples were analyzed for the following water quality variables: pH, total alkalinity, total hardness, conductivity, turbidity, and settleable solids. Hardness and alkalinity were determined using a Hach digital titrator and Hach (1985) methods. Conductivity was measured with a Hach DREL/5 conductivity meter with automatic temperature compensation to 25°C. Conductivity standards were used to check meter performance prior to each measurement series. Measurements of pH were made using an Orion Model SA250 pH meter equipped with a combination electrode and automatic temperature compensation. Prior to each measurement series, two-buffer calibrations were performed using pH buffers accurate to ± 0.02 pH units which bracketed the pH of the samples.

Two measures of solids in water were made. 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). Total settleable solids were measured in triplicate using the Imhoff Cone Method for 1-L samples (APHA et al. 1989). If settleable solids occurred, but did not exceed 0.1 mL/L, "trace" was recorded.

Trace Elements in Sediments

Three composite sediment samples were collected from shallow water at each site. Samples were collected using either a plastic spoon or a stainless steel strainer. Samples were transferred to new acid-cleaned 500-mL I-Chem polyethylene bottles. Fine-grained silt was sought for sampling to allow direct comparison among samples. Each sample bottle was labelled immediately prior to collection and placed in a cooler with ice for transport to a freezer.

Trace Elements in Fish Tissues

Fish were collected by angling, experimental monofilament gillnet, and electroshocker. Target fish species included Arctic grayling (*Thymallus acticus*), Dolly Varden (*Salvelinus malma*), and northern pike; sheefish *(Stenodus leucichthys*), one chum salmon (*Onchorhynchus keta*) and one Alaska blackfish (*Dallia pectoralis*) were also collected. The collection goal was five fish or five composites of fish per sample site. Fish samples were weighed to the nearest gram, and total and fork lengths were measured to the nearest millimeter. Liver, kidney, and muscle samples were dissected, using acid-cleaned stainless steel instruments, from each fresh caught fish longer than 390 mm. A new carbon steel scalpel blade was used for each specimen. Samples were transferred to precleaned 60-mL I-Chem bottles. Small fish (usually <120 mm) from the same site were composited to constitute a sample and analyzed as whole fish, including the gut and gut contents. They also were placed in precleaned I-Chem bottles. Each sample was labelled immediately prior to collection and placed in a cooler with ice for transport to a freezer.

*Laboratory Analyses*

Samples for metals analysis were analyzed by Research Triangle Institute, 3040 Cornwallis Road, Research Triangle Park, NC 27709-2194. Each sediment sample was homogenized by grinding in a Kitchen Aid food processor. Sediment subsamples were freeze dried for determination of moisture content and subsequent acid digestion. Fish tissue samples were homogenized in the original sample containers using a Tekar Tissumizer. For both inductively coupled argon plasma spectroscopy (ICP) and graphite furnace atomic absorption analyses, the freeze-dried subsamples were digested by heating in a water bath in the presence of Baker Instra-Analyzed nitric acid. ICP analyses were conducted using a Leeman Labs Plasma Spec I sequential spectrometer according to Standard Methods (APHA et al. 1989). Arsenic, lead, and selenium were analyzed by flameless atomic absorption spectrophotometry using a graphite furnace. Graphite furnace measurements were made using a Perkin-Elmer Zeeman 3030 atomic absorption spectrophotometer with an HGA-600 graphite furnace and an AS-60 autosampler. Mercury was determined by cold vapor atomic absorption spectrometry using a modification of the method of Hatch and Ott (1968). Samples were wet sieved to determine the proportions of sand (22 mm - 0.0625 mm), silt (0.0625 mm - 0.0039 mm), and clay (<0.0039 mm) (grain size classification parameters are according to Chow 1964).

## *Quality Assurance/Quality Control*

### Field Collections

Sample handling and labelling details are presented in Appendices A and B. Briefly, sampling was conducted following a written study plan containing sample location designations and types of samples to be collected at each site. At the time of collection, samples collected and other pertinent data were recorded in a field notebook. A sample catalog was prepared for each sample matrix prior to submittal of samples to the analytical laboratory. The catalog contained a regional identifier for the sample batch; study objectives; instructions to the laboratory on analyses requested; identification of the detection limits requested; and a tabulated summary of all samples including species, tissue type, collection location, collection date, weight, and other variables.

Prior to data interpretation, field sample identification numbers were converted into a 10-digit identification number, as described in Appendix B. Trace element data for these samples then were entered into a contaminants data management system for northern and interior Alaskan samples. All contaminants data entered into the data management system were proofed by comparing the original data set with a printed copy of the data.

Measurements of pH were performed on the same day as collection. All other water quality variables were measured within 48 hours of collection. Laboratory quality control procedures were followed during analysis of water quality samples. 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.

Sediment sampling followed water sampling and was performed using stainless steel or plastic collection equipment. All sample gear was triple-rinsed in river water at the sample site prior to sampling. Samples were frozen following collection and shipped to the laboratory in coolers with dry ice by overnight air courier.

Fish were rinsed with river water from the site of collection to minimize external contamination. Morphometric measurements were made on site. Dissections of kidney, liver, and dorsal muscle were performed by the collector in the field. Dissections were performed with stainless steel and teflon dissection equipment on a clean surface, with new carbon steel blades. Tissues were immediately placed in storage containers. Samples were shipped to the laboratory in coolers with dry ice by overnight air courier.

Chemical Analyses

Laboratory quality assurance/quality control (QA/QC) procedures, screening criteria to accept or 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, standard reference materials (SRMs), and blanks were used to evaluate data quality. Table 1 identifies acceptable analytical data sets for sediments and fish tissue analyses based on duplicate, spike, SRM and blank criteria, and method limits of detection (LODs). Data were considered acceptable for publication if they met the following criteria: relative percent difference (RPD) of duplicate analyses $\leq$20%, spike recovery 80 - 120%, SRM within $\pm$20% of the certified mean, and mean blank $\leq$15% of the mean duplicate value or <LOD.

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

The analytical laboratory reported that all analyses for aluminum in fish tissue were unacceptable. Replicate C of sediment samples from Site KY4 appears to be anomalously high in beryllium, boron, cadmium, lead, molybdenum, and nickel, when compared with replicates A and B. Also, this replicate was the only detection of molybdenum in the data set. We believe these values are the result of contamination either from the field or the laboratory, and all values from Replicate C were discarded.

*Statistical Analyses*

Values <LOD were replaced by one-half the LOD for statistical analyses. Data sets in which greater than one-half of the values were <LOD were not subjected to statistical analysis. Statistical analyses were performed with SYSTAT statistical software.

Data sets were examined graphically for normality; none satisfied this criterion. Therefore, data set means were compared using non-parametric methods. Ranked data were analyzed using the one-way analysis of variance (for three or more sample sets) and the Student t test (for two sample sets). The Scheffe' multiple range test, a parametric test for pairwise comparisons of means (Sokol and Rohlf 1981), was performed on ranked data to identify differences among specific data sets. Correlations were examined using Pearson product-moment correlations for pairs of variables (Sokol and Rohlf 1981).

Table 1. Acceptable data for metals analysis of sediment and fish tissue, and laboratory method detection limits. U indicates unacceptable data (i.e., poor spike or standard reference material recovery, poor precision within the zone of quantitation, and/or unacceptable levels of blank contamination). NA indicates that the analyte was not included in the laboratory analysis. When either duplicate had a value less than twice the LOD, the precision could not be estimated; these cells are shaded and the corresponding data are considered qualitative.

| Analyte | Method[a] | Sediment (mg/kg) | Tissue (mg/kg) |
|---|---|---|---|
| Aluminum | ICP | U | U |
| Arsenic | AA | NA | 0.5 |
| Barium | ICP | U | NA |
| Beryllium | ICP | 0.2 | 0.1 |
| Boron | ICP | 5 | 5 |
| Cadmium | ICP | 0.2 | 0.1 |
| Chromium | ICP | U | U |
| Copper | ICP | 1 | U |
| Iron | ICP | U | 5 |
| Lead | ICP | 5 | 0.5 |
| Magnesium | ICP | U | 10 |
| Manganese | ICP | 5 | 5 |
| Mercury | AA | 0.14 | 0.1 |
| Molybdenum | ICP | 5 | U |
| Nickel | ICP | 5 | U |
| Selenium | AA | NA | 0.5 |
| Strontium | ICP | 5 | 0.5 |
| Vanadium | ICP | U | U |
| Zinc | ICP | 5 | 1 |

[a] ICP = inductively coupled plasma spectrometry; AA = atomic absorption spectrophotometry.

## RESULTS

### *Water Quality*

Water quality samples were collected between 11-19 June 1991; data are presented in Table 2. All settleable solids measurements were either none or trace, and all samples, except the Sulukna River, had near neutral pH. Turbidity was 8 NTU or less for all sites except Site KY6 (Hogatza River, 17 NTU) and the Site NO2 (Sulatna River, 19 NTU).

Table 2. Water quality measurements at Koyukuk, Northern Unit of Innoko, and Nowitna National Wildlife Refuges, Alaska, 1991.

| Collection Site | Site # | Date | Cond.[a] (µS/cm) | pH | Settleable Solids (mL/L) | Turbidity (NTU) | Total Hardness (mg/L) | Total Alkalinity (mg/L) |
|---|---|---|---|---|---|---|---|---|
| Clear Creek | KY4 | 18 Jun | 30 | 7.1 | 0 | 7 | 3 | 13 |
| Hogatza River | KY6 | 17 Jun | 24 | 7.1 | T | 17 | 0 | 17 |
| Lower Camp Adj. | IN11 | 13 Jun | 165 | 7.2 | T | 3 | 45 | 50 |
| Camp Mine Below | IN12 | 12 Jun | 83 | 7.1 | 0 | 3 | 41 | 44 |
| Camp Mine Above | IN13 | 12 Jun | 75 | 7.3 | 0 | 2 | 61 | 39 |
| Lower Camp Ck. | IN14 | 13 Jun | 66 | 7.0 | 0 | 4 | 21 | 24 |
| Eddy Creek | IN16 | 14 Jun | 78 | 7.2 | 0 | 8 | 36 | 32 |
| Eddy Ck. Adj. | IN17 | 14 Jun | 68 | 7.0 | 0 | 3 | 24 | 26 |
| Sulatna River | NO2 | 19 Jun | 120 | 7.3 | 0 | 19 | 71 | 62 |
| Sulukna River | NO4 | 11 Jun | 218 | 8.3 | 0 | 3 | 125 | 119 |
| Sulukna Adj. | NO7 | 11 Jun | 435 | 7.6 | 0 | 7 | 260 | 267 |

[a] = Conductivity.

The water quality sample from Site KY4 (Clear Creek) was collected at the mouth of the stream. The water quality sample from Site KY6 (Hogatza River) was collected from the Hogatza River at the confluence with Caribou Creek. The sample was a mixture of water from both streams. Water quality at these two sites were very similar. Samples from Clear Creek and the Hogatza River were extremely low in hardness, alkalinity, and conductivity. Hardness and alkalinity values were also low for samples from the Northern Innoko Refuge. Hardness values were 20 mg/L higher above the mine at Camp Creek (Site IN13), a headwater area,

than below (Site IN12). Hardness and alkalinity values from above and below the mine at Camp Creek were greater than values of these variables from the lower reaches of the stream.

Values of conductivity, pH, turbidity, hardness, and alkalinity in samples from the Nowitna River drainage (Sites NO2, NO4, and NO7) were the greatest of all rivers and creeks. Samples from Site NO7 (Sulukna Adj. Pond) had the highest values of conductivity, hardness, and alkalinity (435 µS/cm, 260 mg/L, and 267 mg/L, respectively).

### *Trace Elements in Sediments*

All contaminant concentrations in sediment are expressed as mg/kg dry weight. QA/QC screening indicated that beryllium, boron, cadmium, copper, lead, manganese, mercury, molybdenum, nickel, strontium, and zinc results were acceptable (Table 1, Appendix E). Concentrations of frequently detected metals are shown in Table 3. Beryllium was detected at all sample sites except Site IN13 (Camp Creek above mine), in concentrations ranging from <0.20 to 1.54 mg/kg. The greatest beryllium concentrations were at the Koyukuk Refuge. Boron was detected in concentrations from <5.00 to 11.30 mg/kg, most consistently at the Northern Innoko Refuge. Cadmium concentrations ranged from <0.20 mg/kg to 1.30 mg/kg. Copper, lead, nickel, strontium, and zinc were detected in each sample. Mean copper, nickel, and zinc concentrations in the Northern Innoko Refuge were significantly greater than in the Koyukuk and Nowitna refuges ($F_{2,33} = 11.3$, $P < 0.01$; $F_{2,33} = 28.5$, $P < 0.01$; $F_{2,33} = 6.2$, $P = 0.05$, respectively). Also, nickel concentrations of Koyukuk Refuge samples were significantly greater than those from Nowitna Refuge ($F_{2,33} = 28.5$, $P < 0.01$). Mercury and molybdenum were not detected in any sample (LODs = 0.14 mg/kg and 5.00 mg/kg, respectively). Mean values, by refuge, of beryllium, boron, cadmium, copper, lead, manganese, and nickel were lowest from the Nowitna Refuge. The greatest mean concentration of zinc was found in sediments from Site IN14 (129 mg/kg).

Copper, nickel, strontium, and zinc concentrations differed among sample sites. Copper concentrations were significantly lower at Sites KY6 (Hogatza River), NO4 (Sulukna River), and NO7 (Sulukna River adjacent) than at Sites IN14 (Lower Camp Creek) and IN17 (Eddy Creek lake) ($F_{11,24} = 8.6$, $P < 0.001$). Nickel concentrations at Site IN13 were significantly greater than at Sites KY6, NO2 (Sulatna River), NO4 (Sulukna River), and NO7 (Sulukna Adj. Pond) ($F_{11,24} = 10.4$, $P < 0.05$). Also, nickel concentrations were significantly greater at Sites IN12 (Camp Creek downstream of mine), IN14, and IN17 than at Site NO4 ($F_{11,24} = 10.4$, $P < 0.05$). Thirty significant differences occurred among sites for strontium concentrations. Sites NO4 and NO7 had greater concentrations of strontium than most other sites, and Sites IN12 and IN13 had lower strontium concentrations than most other sites ($F_{11,24} = 34.3$, $P < 0.05$). Twenty significant differences occurred among sites for zinc concentrations. In general, samples from the Northern Innoko Refuge had significantly greater zinc concentrations than those from the Koyukuk and Nowitna refuges ($F_{11,24} = 18.1$, $P < 0.05$), with the notable exception of Site NO6.

Table 3. Mean metal concentrations in sediment from Koyukuk, Northern Unit of Innoko, and Nowitna National Wildlife Refuges. Each concentration is the mean of three replicate samples.

| | Grain Size (%) | | | Metals Concentrations (mg/kg dry weight) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Site | Clay | Silt | Sand | Be | B | Cd | Cu | Pb | Mn | Ni | Sr | Zn |
| KY4[a] | 1.7 | 50 | 48 | 0.79 | <5.00[b] | 0.74 | 29.2 | 22.1 | 542 | 34.8 | 27.0 | 83 |
| KY6 | 0.2 | 69 | 31 | 0.82 | 7.31[c] | 0.62 | 25.1 | 12.2 | 469 | 30.9 | 22.5 | 68 |
| Koyukuk Refuge | | | | 0.81 | -[d] | 0.68 | 27.2 | 17.2 | 506 | 32.9 | 24.8 | 75 |
| IN11 | 0.4 | 13 | 85 | 0.61 | 8.50 | 0.92 | 37.6 | 16.6 | 676 | 38.6 | 32.4 | 86 |
| IN12 | 0.3 | 58 | 39 | 0.27 | 5.97[c] | 0.40 | 30.9 | 14.9 | 778 | 46.9 | 19.3 | 73 |
| IN13 | 0.1 | 11 | 87 | <0.20[d] | <5.00 | 0.87 | 35.4 | 12.0 | 1097 | 78.2 | 11.8 | 105 |
| IN14 | 0.2 | 31 | 67 | 0.50 | 7.73[c] | 0.63 | 40.4 | 13.4 | 460 | 41.8 | 27.4 | 129 |
| IN16 | 0.4 | 90 | 9 | 0.46 | 5.32 | 0.43 | 31.8 | 14.5 | 571 | 37.3 | 30.6 | 96 |
| IN17 | 0.3 | 33 | 64 | 0.51 | 5.63 | 0.58 | 41.2 | 11.8 | 513 | 41.1 | 35.9 | 106 |
| N. Innoko Refuge | | | | 0.40 | -[d] | 0.59 | 36.2 | 13.9 | 683 | 47.3 | 26.2 | 99 |
| NO2 | 0.4 | 85 | 15 | 0.33 | <5.00 | 0.22 | 27.2 | 10.3 | 613 | 29.1 | 26.2 | 81 |
| NO4 | 0.1 | 43 | 57 | 0.29 | 4.81 | 0.20 | 19.3 | 9.8 | 455 | 25.2 | 53.6 | 61 |
| NO6 | 0.1 | 36 | 61 | 0.49 | 6.00[c] | 0.45 | 35.7 | 14.5 | 253 | 33.5 | 21.1 | 122 |
| NO7 | 0.3 | 76 | 24 | 0.31 | <5.00 | <0.20 | 24.7 | 12.1 | 672 | 27.3 | 58.7 | 74 |
| Nowitna Refuge | | | | 0.35 | -[d] | 0.24 | 26.7 | 11.7 | 498 | 28.8 | 39.9 | 84 |
| Mean of all samples | | | | 0.44 | -[d] | 0.48 | 31.6 | 13.6 | 593 | 38.8 | 30.7 | 91 |

[a] n = 2.
[b] The < indicates that all replicate sample analyses were <LOD.
[c] Figure represents the only detection >LOD.
[d] Greater than 50% of the samples were <LOD.

Samples from Site IN13 (Camp Creek above mine) contained significantly greater zinc than samples from Site IN12 (Camp Creek below mine) ($F_{11,24} = 18.1$, $P < 0.05$). Concentrations of metals from paired river/river-adjacent sites (Site NO2 and NO6; Site IN14 and Site IN11; and Site NO4 and Site NO7) were not significantly different ( $P > 0.90$ in almost all comparisons, indicating very little difference between sites).

The clay fraction (<0.0039 mm) of all samples, except KY4 rep. B, was <0.6%. Percentages of sand (0.0039 mm to 0.0625 mm) in samples ranged from 6% to 93% and percentages of silt (>0.0625 mm to 22 mm) ranged from 7% to 92%. Percentages of clay, silt, and sand in samples were not correlated with concentrations of metals.

*Trace Elements in Fish Tissues*

All contaminant concentrations in tissue are expressed as mg/kg dry weight. QA/QC screening indicated that arsenic, beryllium, boron, cadmium, iron, lead, magnesium, manganese, mercury, selenium, strontium, and zinc results were acceptable (Table 1, Appendices F and G). Kidney, liver, and muscle samples were collected from 2 Arctic grayling, 31 northern pike, and 6 sheefish (n = 112). From Site IN12 (Camp Creek downstream of placer mine), 27 whole Dolly Varden were collected and composited to create 3 samples. One whole Alaska blackfish and kidney, liver and muscle samples from one chum salmon also were collected.

Concentrations of frequently detected metals are shown in Table 4. Arsenic was detected in three muscle samples of northern pike from the Koyukuk and Northern Innoko refuges: one sample from Site KY6 (Hogatza River) at 8.1 mg/kg and two samples from Site IN14 (Lower Camp Creek) at concentrations near the LOD (0.5 mg/kg). Arsenic was detected in 11 of 43 kidney, liver, and muscle samples from the Nowitna Refuge in concentrations up to 1.6 mg/kg. Boron was detected in six tissue samples in concentrations up to 3.65 mg/kg. Beryllium was detected at each sample site except Site IN11 (Lower Camp Creek adjacent) where the sole Alaska blackfish was collected. Beryllium was detected sporadically and concentrations were greatest, up to 1.86 mg/kg, in Dolly Varden collected at Site IN12 (Camp Creek below the mine). Lead was detected in five samples: in a whole body composite sample of Dolly Varden from Site IN12 (Camp Creek downstream), in two northern pike (one each from Sites NO6 [Sulatna River adjacent] and IN16 [Eddy Creek]), and in one sheefish liver and one sheefish kidney from Site NO4 (Sulukna River).

Iron was detected in all but five samples in concentrations ranging from <5.00 to 2210 mg/kg. Mercury was detected in all but one tissue sample (LOD = 0.10 mg/kg). Eighteen samples met or approached 4.00 mg/kg of mercury. These tissues were collected from three sheefish and six northern pike on the Koyukuk and Nowitna refuges. The highest mercury concentration in tissue from the Northern Innoko Refuge was 3.09 mg/kg from a northern pike kidney at Site IN16 (Eddy Creek). Magnesium, selenium, and zinc were detected in each sample. Mean magnesium concentrations ranged from 389 mg/kg in a northern pike liver at

Table 4. Mean metals concentrations of kidney, liver, muscle and whole body of fish from Koyukuk, Northern Unit of Innoko, and Nowitna National Wildlife Refuges, Alaska, 1991.

| | | | | | mg/kg dry weight | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Site | N | Species[a] | Tissue[b] | Date | Cd | Fe | Hg | Mg | Mn | Se | Zn |
| KY4 | 1 | AG | K | 18 Jun | <0.10 | | 0.76 | | | | |
| KY4 | 4 | NP | K | 18 Jun | 0.47 | 327 | 3.20 | 649 | 2.43 | 10.30 | 587 |
| KY6 | 5 | NP | K | 19 Jun | 0.44 | 328 | 5.07 | 719 | 3.69 | 9.97 | 633 |
| IN14 | 2 | NP | K | 13 Aug | 0.28 | 479 | 1.11[c] | 403 | 3.64 | 6.57 | 852 |
| IN16 | 4 | NP | K | 30 Aug | 0.20 | 509 | 1.51[c] | 684 | 3.22 | 7.05 | 1018 |
| IN17 | 1 | NP | K | 14 Jun | 0.55 | 357 | 0.90[d] | 752 | 0.50 | 7.00 | 835 |
| NO2 | 1 | CH | K | 28 Aug | 8.81 | 714 | 0.30 | 618 | 3.92 | 8.21 | 105 |
| NO2 | 4 | NP | K | 28 Aug | 0.64 | 822 | 1.07 | 781 | 4.86 | 6.16 | 395 |
| NO4 | 5 | SH | K | 21 Aug | 0.79 | 1025 | 4.38 | 614 | 3.63 | 7.50 | 208 |
| NO6 | 1 | NP | K | 19 Jun | 1.64 | 250 | 0.44[e] | 707 | 4.36 | 6.10 | 485 |
| KY4 | 1 | AG | L | 19 Jun | | | 0.43 | | | | |
| KY4 | 4 | NP | L | 19 Jun | 0.16 | 1119 | 1.95 | 419 | 5.02 | 6.51 | 133 |
| KY6 | 5 | NP | L | 19 Jun | 0.15 | 903 | 3.16 | 491 | 4.73 | 7.09 | 175 |
| IN14 | 5 | NP | L | 13 Aug | 0.13 | 910 | 0.58 | 461 | 5.03 | 5.86 | 176 |
| IN16 | 5 | NP | L | 30 Aug | <0.10[f] | 522 | 0.68 | 476 | 3.19 | 6.33 | 172 |
| IN17 | 3 | NP | L | 14 Jun | <0.10 | 683 | 0.36 | 389 | 3.20 | 4.20 | 181 |
| NO2 | 1 | CH | L | 28 Aug | 4.96 | 639 | 0.30 | 521 | 7.80 | 18.10 | 270 |
| NO2 | 5 | NP | L | 28 Aug | <0.10[g] | 308 | 0.49 | 429 | 2.81 | 4.69 | 248 |
| NO4 | 1 | NP | L | 11 Jun | 0.14 | 462 | 1.43 | 318 | 2.00 | 5.00 | 63 |
| NO4 | 5 | SH | L | 21 Aug | 0.16 | 542 | 2.58 | 858 | 5.05 | 4.97 | 99 |
| NO6 | 1 | NP | L | 20 Jun | 0.91 | 252 | 1.25[d] | 821 | 0.50 | 7.42 | 290 |
| KY4 | 1 | AG | M | 18 Jun | <0.10 | 52 | 0.56 | 947 | 0.50 | 1.75 | 18 |
| KY4 | 4 | NP | M | 18 Jun | <0.10 | 17 | 3.00 | 1137 | 4.07 | 1.65 | 18 |
| KY6 | 5 | NP | M | 19 Jun | <0.10 | 29 | 3.45 | 1500 | <1.00[h] | 1.74 | 21 |

Table 4 Cont.

| Site | N | Species | Tissue | Date | Cd | Fe | Hg | Mg | Mn | Se | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| IN14 | 5 | NP | M | 13 Aug | 0.21 | 18 | 1.72 | 1218 | 3.51 | 1.17 | 19 |
| IN16 | 5 | NP | M | 30 Aug | <0.10 | 50 | 1.64 | 1255 | <1.00[i] | 1.04 | 24 |
| IN17 | 3 | NP | M | 14 Jun | <0.10 | 16 | 1.32 | 984 | 2.01 | 0.75 | 20 |
| NO2 | 1 | CH | M | 28 Aug | <0.10 | 58 | 0.21 | 824 | 0.50 | 1.95 | 20 |
| NO2 | 5 | NP | M | 28 Aug | <0.10 | 31 | 1.67 | 1206 | 1.91 | 1.16 | 19 |
| NO4 | 1 | NP | M | 11 Jun | <0.10 | 14 | 3.63 | 1089 | 1.00 | 1.18 | 16 |
| NO4 | 5 | SH | M | 21 Aug | <0.10 | 29 | 2.77 | 1029 | 1.20 | 1.38 | 14 |
| NO6 | 3 | NP | M | 19 Jun | <0.10 | 8 | 1.87 | 1064 | 2.29 | 0.57 | 20 |
| | | | | | | | | | | | |
| IN11 | 1 | AB | W | 13 Jun | <0.10 | 413 | 0.05 | 1500 | 22.80 | 1.32 | 273 |
| IN12 | C[j] | DV | W | 12 Jun | 0.36 | 347 | 0.18 | 816 | 20.60 | 6.68 | 122 |
| IN12 | C | DV | W | 12 Jun | 0.38 | 307 | 0.15 | 741 | 15.60 | 5.53 | 120 |
| IN12 | C | DV | W | 12 Jun | 0.32 | 244 | 0.15 | 683 | 12.40 | 5.67 | 116 |

[a] CH = chum salmon (*Oncorhynchus keta*), SH = sheefish (*Stenodus leucichthys*), NP = northern pike (*Esox lucius*), AG = Arctic grayling (*Thymallus arcticus*), AB = Alaska blackfish (*Dallia pectoralis*), DV = Dolly Varden (*Salvelinus malma*).
[b] K = kidney, L = liver, M = muscle.
[c] n = 5.
[d] n = 3.
[e] n = 2.
[f] All samples contained ≤0.11 mg/kg.
[g] Three of five samples were ≤0.10; the other two samples contained 0.13 mg/kg and 0.57mg/kg.
[h] Three of five samples were <LOD; the other two samples contained 2.42 mg/kg and 3.23 mg/kg.
[i] Three of five samples were <LOD; the other two samples contained 5.30 mg/kg and 3.22 mg/kg.
[j] Composite samples composed of whole fish.

Site IN17 (Eddy Creek adjacent) to 2985 mg/kg in a northern pike muscle sample at Site KY6 (Caribou Creek).

Selenium concentrations varied considerably among sites, ranging from 0.51 mg/kg in a northern pike muscle sample to 18.01 mg/kg in the chum salmon liver. Mean selenium concentrations for kidney, liver, and muscle in northern pike were 8.1 mg/kg, 5.9 mg/kg, and 1.2 mg/kg, respectively. Zinc concentrations ranged from 18 mg/kg to 1018 mg/kg, and accumulated primarily in kidney and liver.

Significant differences in metals concentrations of kidney, liver, and muscle tissue of northern pike, by refuge, are listed in Table 5. Mercury in fish tissue was significantly greater at the Koyukuk Refuge than in Northern Innoko and Nowitna refuges for all tissue types ($F_{2,23}$ =

14.3, $P < 0.0001$). The mean concentrations of mercury in kidney tissue at these refuges were 4.37 mg/kg, 1.24 mg/kg, and 0.86 mg/kg, respectively. Selenium concentrations in kidney and muscle were significantly higher at the Koyukuk Refuge than at the Northern Innoko and Nowitna refuges ($F_{2,18} = 23.3$, $P < 0.0001$). Cadmium concentrations in fish did not differ significantly among refuges.

In 9 of 21 comparisons, metal concentrations in northern pike and sheefish differed significantly (Table 6). Cadmium and mercury concentrations in northern pike kidney were significantly greater than in sheefish kidney ($F_{1,27} = 7.3$, $P < 0.05$ and $F_{1,29} = 6.6$, $P < 0.05$, respectively). Mercury concentrations in sheefish liver were significantly greater than in northern pike liver ($F_{1,34} = 9.1$, $P < 0.01$). Zinc concentrations were greater in northern pike than in sheefish in all three tissues (kidney: $F_{1,24} = 17.0$, $P < 0.001$; liver: $F_{1,32} = 4.3$, $P < 0.05$; muscle: $F_{1,34} = 17.3$, $P < 0.001$). Concentrations of mercury in muscle did not differ significantly between the two species.

Table 5. Significant differences in metals concentrations of kidney, liver, and muscle tissue from northern pike (*Esox lucius*) from Koyukuk, Northern Unit of Innoko, and Nowitna National Wildlife Refuges, Alaska, 1991. Differences were determined using the ANOVA and Scheffe' tests on ranked data. A blank indicates no significant difference.

| Tissue | N | Cd | Fe | Hg | Mg | Mn | Se | Zn |
|---|---|---|---|---|---|---|---|---|
| Kidney | 21 | | IN, NO>KY[a] | KY>IN,NO | | | KY>IN,NO | IN>KY,NO |
| Liver | 29 | | IN, KY>NO | KY>IN,NO | | KY>NO | | |
| Muscle | 30 | [b] | | KY>IN,NO | | | KY>IN,NO | |

[a] IN = Northern Innoko Refuge, NO = Nowitna Refuge, and KY = Koyukuk Refuge.
[b] Data were insufficient to conduct a test.

When concentrations of metals in kidney, liver, and muscle tissue were compared, for northern pike and sheefish , the partitioning of iron, selenium, and zinc among tissues had the same pattern for both species (Table 7). The pattern was also similar for cadmium. Northern pike muscle had significantly lower concentrations of all metals except magnesium and mercury. Mercury concentrations in kidney and muscle of northern pike were significantly greater than in liver ($F_{2,85} = 9.12$, $P < 0.01$).

Nine significant differences occurred among sites regarding metals concentrations in kidney, liver, and muscle of northern pike (Table 8). Magnesium and manganese concentrations did not differ significantly among sites. No significant differences in metals concentrations among sites were detectable for liver. No two sites within a drainage differed significantly from one another.

Table 6. Significant differences in metals concentrations of kidney, liver, and muscle tissue in northern pike (*Esox lucius*) versus sheefish (*Stenodus leucichtys*) from Koyukuk, Northern Unit of Innoko, and Nowitna National Wildlife Refuges, Alaska, 1991. Differences were determined using the ANOVA and Scheffe' tests on ranked data. A blank indicates no significant difference.

| Tissue | N | Cd | Fe | Hg | Mg | Mn | Se | Zn |
|---|---|---|---|---|---|---|---|---|
| Kidney | 26 | SH>NP[a] | SH>NP | NP>SH | [b] | | | NP>SH |
| Liver | 34 | | | SH>NP | SH>NP | SH>NP | | NP>SH |
| Muscle | 35 | [b] | | | | | | NP>SH |

[a] SH = Sheefish, NP = Northern Pike.
[b] Data were insufficient to conduct a test.

Table 7. Significant differences in metal concentrations of kidney, liver, and muscle tissue from northern pike (*Esox lucius*) and sheefish (*Stenodus leucichthys*) collected from Koyukuk, Northern Unit of Innoko, and Nowitna National Wildlife Refuges, Alaska, 1991. Differences were determined using the ANOVA and Scheffe' tests on ranked data. A blank indicates no significant difference among tissues.

| Species | N | Cd | Fe | Hg | Mg | Mn | Se | Zn |
|---|---|---|---|---|---|---|---|---|
| Northern Pike | 80-88 | K>L>M | K,L>M | K,M>L | M>K>L | L>M | K>L>M | K>L>M |
| Sheefish | 15 | K>L,M | K,L>M | [a] | | K>M | K>L>M | K>L>M |

[a] Data were insufficient to conduct a test.

Table 8. Significant differences by site in metal concentrations of kidney, liver, and muscle tissue from northern pike (*Esox lucius*) collected from Koyukuk, Northern Unit of Innoko, and Nowitna National Wildlife Refuges, Alaska, 1991. Differences were determined using the ANOVA and Scheffe' tests on ranked data.

| Tissue | N | Cd | Fe | Hg | Mg | Se | Zn |
|---|---|---|---|---|---|---|---|
| Kidney | 21-26 | [a] | NO2>KY6 | KY6>NO6 | | KY6>NO2 | NO2>IN16 |
| Liver | 29-31 | | [b] | [b] | | | |
| Muscle | 30-31 | [c] | | | | KY4>IN16, IN17; KY6>IN16, IN17, NO6 | |

[a] A blank indicates no significant difference among sites.
[b] A significant difference occurred, however, the Scheffe' procedure did not identify which sites differed.
[c] Data were insufficient to conduct a test.

## DISCUSSION

### *Water Quality*

Water quality data are valuable for characterizing waterbodies and for evaluating other aquatic-based data; however, due to daily and seasonal variations, comparisons of water quality data collected during different time periods can be used for discussion of general trends only. The streams sampled during this study had soft water and were calcium and magnesium bicarbonate-dominated. All waterbodies sampled had near neutral pH except for the Sulukna River and the Sulukna Adjacent Pond which were higher in pH. Based on the close relationship between hardness and alkalinity values, sulfates, the second most concentrated anion component in streams from other areas of Alaska (D. Snyder, U.S. Geological Survey, pers. comm.), if present, were present in low concentrations.

Values of water quality variables at Clear Creek (Site KY4) and the Hogatza River (Site KY6), on the Koyukuk Refuge, are similar to those measured during June 1987 except for pH and only slightly different from those measured during June 1988 except for pH at Clear Creek (Snyder-Conn et al. 1992a). Values of pH were more basic during 1991 than during 1987 and 1988 (Snyder-Conn et al. 1992a); however, all values are within the range typical of interior Alaska rivers (Snyder-Conn et al. 1992a,b; Mueller et al. 1995). Hardness values at Clear Creek and the Hogatza River measured during 1991 were extremely low for unknown reasons.

Clear Creek was slightly turbid (7 NTU) during the sample collection period due to natural rapid erosion of a bank upstream of the sample site. Based on daily measurments from 22 June to 21 July 1995, Headlee (1996a) reported the mean turbidity of Clear Creek as 2.1 NTU (range = 0.7 - 4.8 NTU). He reported settleable solids as either trace or undetectable for the sample period. Van Hatten (pers. comm) conducted daily measurements of turbidity and pH from 22 June to 20 July 1996. The mean turbidity for this period was 6.0 NTU (range = 3.3 to 20 NTU) and the mean pH was 7.46 (mean = 6.93 to 7.88). His highest turbidity values were measured after a significant rainstorm of 4.3 cm and turbidity values returned to the baseline level, approximately 4 NTU, after five days (K. Van Hatten pers. comm) .

The U.S. Fish and Wildlife Service (unpublished data) measured water quality variables in 1984 at: Bering Creek, a tributary of the Yukon River upstream of the Nowitna River, within the Nowitna Refuge; the Sulatna River, one mile upstream of the confluence with the Nowitna River; the Titna River, at the confluence with the Nowitna River; California Creek, a tributary of the Titna River; the Nowitna River, above the confluence with the Titna River; and the Hogatza River, at the confluence with the Koyukuk River, at the Koyukuk Refuge boundary. The results are in Table 9.

Caribou Creek was extremely turbid during our sample period, due to bucket dredge placer mining occurring upstream of the sample site. However, the sample from the Hogatza River

Table 9. Water quality data collected at Nowitna and Koyukuk National Wildlife Refuges, Alaska, 1984.

| Site | Date | Cond. µS/cm | pH | S.S. mL/L | Turbidity NTU | Hardness mg/L | Alkalinity mg/L |
|---|---|---|---|---|---|---|---|
| Bering Creek | June | 180 | 7.0 | T | 9 | 86 | 86 |
| | Sept. | 470 | 7.5 | T | 205 | 206 | 240 |
| Sulatna R. | June | 74 | 6.5 | T | 21 | 34 | 34 |
| | Sept. | 240 | 7.0 | T | 40 | 103 | 120 |
| Titna R. | June | 130 | 7.5 | 0.3 | 19 | 69 | 69 |
| Califomia Creek | June | 290 | 8.0 | T | 9 | 137 | 154 |
| Nowitna R. | June | 110 | 7.5 | 0.3 | 28 | 69 | 69 |
| | Sept. | 310 | 7.5 | T | 7 | 120 | 137 |
| Hogatza R. | June | 75 | 8.0 | T | 6 | 51 | 51 |
| | Sept. | 86 | 7.0 | T | 6 | 69 | 69 |

(Site KY6) was collected from an eddy at the mouth of Caribou Creek which was primarily composed of Hogatza River water and thus, it is more characteristic of that waterway.

Hardness, alkalinity, and conductivity values measured at the mouth of the Hogatza River in June and September 1984 (U.S. Fish and Wildlife Service, unpublished data) and were slightly greater than those measured in June 1987 and similar to those measured in June 1988 (Snyder-Conn et al. 1992a), but still moderately low and within the normal range for interior Alaskan rivers (Snyder-Conn et al. 1992a,b; Mueller et al. 1995). Values of pH measured by Snyder-Conn et al. (1992a) at the mouth of the Hogatza River and Caribou Creek for 1987 and 1988 were all basic. Values of pH at Caribou Creek from our study and September 1984 at the mouth of the Hogatza River (U.S. Fish and Wildlife Service, unpublished data) were neutral. Other water quality variables measured during 1991 from the Hogatza River at Caribou Creek are similar to those measured by Snyder-Conn et al. (1992a) at the mouth of the Hogatza River in 1987 except that the turbidity was higher at the mouth of the river.

The Clear Creek and Caribou Creek watersheds constitute some of the most productive chum salmon spawning habitat within the Koyukuk River drainage and have been designated an Area of Critical Environmental Concern by the U.S. Bureau of Land Management (Kretsinger et al. 1994). Headlee (1996a) and Van Hatten (pers. comm.) reported counting 116,735 and 101,250 summer chum salmon migrating toward spawning areas in the Clear Creek drainage during 1995 and 1996, respectively. Turbidity, suspended solids, and increased bed load can have devastating effects on fish habitat. Increased turbidity is associated with reduced light penetration and primary productivity (Van Nieuwnhuyse and LaPerriere 1986), decreased abundance of fish food organisms, decreased production and abundance of fish (Sigler et al. 1984, Lloyd et al. 1987), and feeding behavioral changes in coho salmon (*Oncorhynchus kisutch*) (Berg and Northcote 1985) and Arctic grayling (Scannell 1988). Sedimentation due to placer mining has been shown to decrease the density and biomass of aquatic invertebrates

(Wagener and LaPerriere 1985), and drastically reduce the overall production of salmon by reducing egg and embryo survival (Crouse et al. 1981). Placer mining also has been shown to significantly increase concentrations of total arsenic, copper, lead, and zinc, and dissolved arsenic and zinc in water (LaPerriere et al. 1985). Barton (1984) observed that the substrate within Bear Creek, a tributary to Caribou Creek, and Caribou Creek, downstream of the confluence of Bear Creek, was very embedded and heavily compacted due to placer mining on Bear Creek.

Eddy Creek (Site IN16), Lower Camp Creek (Site IN14) (both from 1991 data) and Bonanza Creek (data from 1987-1988), all of which flow into Kaiyuh Flats, have similar water quality values, except that Bonanza Creek from 1988 had moderately higher conductivity, hardness, and alkalinity (Snyder-Conn et al. 1992a). Headlee (1996b) reported a similar pH value on Eddy Creek, several miles downstream of Site IN16, as we measured in 1991. However, his pH measurements at Bonanza, American/North, and Bishop creeks, also tributaries to Kaiyuh Flats, were >7.6, greater than ours from Kaiyuh Flats, possibly a result of his sampling later in the summer than we did. Headlee (1996b) also reported hardness and conductivity measurements much greater than in our study. Lower water flow rates during his August sampling period and evaporative concentration throughout the summer are possible causes for these differences. In all cases, the U.S. Fish and Wildlife Service (unpublished data) measured greater values of conductivity, hardness, and alkalinity in September than in June.

The inactive placer mine at Camp Creek apparently had little effect on water quality downstream of the mine. Water quality variables measured above and below the Camp Creek mine (Sites IN12 and IN13, respectively) were comparable except that hardness was 20 mg/L greater above the mine. This mine was not in operation nor had it been for several years prior to sampling.

The pH of the Sulatna River (Site NO2) was similar to those measured during August 1987 and 1988 at the Nowitna Refuge boundary (Snyder-Conn et al. 1992b), and greater than the pH measured during June and September, 1984, 1.5 kilometers upstream of the mouth of the Sulatna River (U.S. Fish and Wildlife Service, unpublished data). Hardness, alkalinity, and conductivity values from our study were less than during 1988 at the Nowitna Refuge boundary (Snyder-Conn et al. 1992b) and approximately midway between the June and September values determined by U.S. Fish and Wildlife Service (unpublished data). Values of hardness and alkalinity in our study are greater than from 1985 at the mouth of the Sulatna River, but the turbidity values are identical (Snyder-Conn et al. 1992b). Turbidity measurements of the Sulatna River during 1987 and 1988 were far greater than during 1985 (Snyder-Conn et al. 1992b), or our study, but similar to and less than from June and September 1984, respectively (U.S. Fish and Wildlife Service, unpublished data). Snyder-Conn et al. (1992b) and Alt (1985) attributed high turbidities in the Sulatna River to placer mining activity. Based on our turbidity measurement of 19 NTU for this waterway, we conclude that placer mining discharges similar to those causing high turbidities in prior years, up to 3467 NTU (Snyder-Conn et al. 1992b), were not occurring during our sample period.

Sulukna Adj. Pond (Site NO4) had high values of conductivity, hardness, and alkalinity likely due to evaporative concentration in the pond. The pond was possibly ephemeral, very shallow, and had a large surface-to-volume ratio enhancing evaporative concentration.

*Trace Elements in Sediments*

In general, concentrations of beryllium, cadmium, lead, and mercury in sediment samples were characteristic of uncontaminated sediments (Moore and Ramamoorthy 1984; Bennett and Cubbage 1991; CCME 1991; Persaud et al. 1992; Outridge et al. 1994). Concentrations of mercury greater than 0.30 mg/kg have been found in stream silt from drainages of the upper Sulukna River (King et al. 1983); however, all samples from our study had <0.14 mg/kg mercury. Although greater than in other studies (Mueller et al. 1993; Eppenger et al. 1994), copper and zinc concentrations from our study seem to be within the normal range for Northern Innoko, Nowitna, and Koyukuk refuges. Nickel concentrations also appear to be within the normal range for these refuges.

Mean concentrations of cadmium and lead were greatest at the Koyukuk Refuge, and mean concentrations of copper, manganese, nickel, and zinc were greatest at the Northern Innoko Refuge. Concentrations of beryllium, cadmium, copper, lead, manganese, and nickel in sediment samples were lowest from the Nowitna Refuge.

Mean beryllium concentrations from Koyukuk refuge samples, 0.79 mg/kg and 0.82 mg/kg, are twice as high as those from the same sites in 1988 (Snyder-Conn et al. 1992a). The maximum mean beryllium concentration of 37 sites from Kanuti National Wildlife Refuge, upstream of the Koyukuk Refuge on the Koyukuk River, was 0.23 mg/kg (Mueller et al. 1995). Mean beryllium concentrations from Nowitna Refuge during 1987 (Snyder-Conn et al. 1992b) were approximately four times greater, up to 1.38 mg/kg, than at the same sites in 1991 or 1988 (Snyder-Conn et al. 1992b). CCME (1991) lists 4.0 mg/kg as a background concentration for beryllium in sediment.

Several investigators list lead concentrations of 23-50 mg/kg as background conditions (Moore and Ramamoorthy 1984, Bennett and Cubbage 1991, CCME 1991, Persaud et al. 1992). Mean lead concentrations at Kanuti and Koyukuk refuges have been reported as 7.4 mg/kg (Mueller et al. 1995) and 13.1 mg/kg (Snyder-Conn et al. 1992a), respectively. Mean lead concentrations from our study were 9.8 - 22.1 mg/kg. Eppenger et al. (1994) reported a mean lead concentration of 8.8 mg/kg in stream and pond sediments at the Koyukuk Refuge.

Concentrations of copper, nickel, and zinc were significantly greater from the Northern Innoko Refuge than from the Koyukuk and Nowitna refuges. Copper concentrations exceeded those listed as background conditions by other investigators (Moore and Ramamoorthy 1984, Bennett and Cubbage 1991, CCME 1991, Persaud et al. 1992) at all Northern Innoko and Koyukuk refuge sites, and at two of four sites at Nowitna Refuge. Copper concentrations from our study were not significantly different from those reported for Kanuti (Mueller et al. 1995), Koyukuk (Snyder-Conn et al. 1992a), and Nowitna (Snyder-

Conn et al. 1992b) refuges. Copper concentrations from Selawik Refuge, bordering the Koyukuk Refuge on the northwest, were far lower (Mueller et al. 1993) than from Koyukuk, Nowitna, and Kanuti refuges. Eppenger et al. (1994) reported mean copper concentrations in stream and pond sediments of the Koyukuk Refuge similar to those from our study.

Concentrations of nickel in sediment appear to be high throughout the central portion of the Interior of Alaska. Nickel concentrations exceeded those reported as background conditions (Moore and Ramamoorthy 1984, Bennett and Cubbage 1991, CCME 1991, Persaud et al. 1992) at all sample sites, except Sulukna River (Site NO4) and Sulukna River Adjacent (Site NO7). However, nickel concentrations from Koyukuk and Nowitna refuges are similar to those reported from other studies at these refuges (Snyder-Conn et al. 1992a,b) and the Kanuti Refuge (Mueller et al. 1995). Nickel concentrations from our study were greatest at the Northern Innoko Refuge.

Background concentrations of zinc range from 50 mg/kg (Moore and Ramamoorthy 1984) to 100 mg/kg (Bennett and Cubbage 1991, CCME 1991, Persaud et al. 1992). The mean zinc concentration from all sites in our study was 91 mg/kg. Eppenger et al. (1994) reported a mean zinc concentration of 60.4 mg/kg in stream and pond sediments of the Koyukuk Refuge. Mean zinc concentrations from other studies in these and adjacent National Wildlife Refuges were not significantly different from those of our study (Snyder-Conn et al. 1992a,b; Mueller et al. 1993, 1995).

Cadmium concentrations were more than twice as great above the Camp Creek mine (Site IN12) as below (Site IN13). Similarly, zinc concentrations were significantly greater above the mine than below. In general, sediment samples from mined streams did not have greater concentrations of metals than those from unmined streams.

### *Trace Elements in Fish Tissues*

Arctic grayling, northern pike, and sheefish are migratory species (Morrow 1980; Alt 1985, 1987) and, thus, assigning the origin of contaminants found in these species is difficult, if not impossible. Radio-tagged Arctic grayling have been documented to migrate up to 101 km from spawning or summer feeding areas to overwintering sites (West et al. 1992). Northern pike generally spend the winter in deepwater areas and in spring move upstream to spawning and summer feeding areas (Morrow 1980). Alt (1985) reported that northern pike generally do not migrate off of Nowitna Refuge by way of the Yukon River. On Kaiyuh Flats, Taube (1995) determined that radio-tagged northern pike remained in Kaiyuh Flats all year. He identified three overwintering areas. These fish left overwintering areas in March and early April bound for spawning areas. Sheefish winter in downstream areas and spawn in upstream areas (Morrow 1980). Nowitna River sheefish are a separate nonanadromous stock although some overlap of range occurs with the anadromous stocks of the lower Yukon River (Alt 1987). Nowitna River sheefish overwinter in the lower Nowitna River or in the Yukon River in the vicinity of the Nowitna River mouth. Sheefish migrate into the Nowitna River from overwintering areas soon after breakup and disperse into feeding areas. Peak migration is in

late May and early June. Movement of sheefish up the Sulukna River to spawning grounds in the Sulukna River occurs throughout September. After spawning, sheefish migrate downstream and probably arrive at the mouth of the Nowitna River by late October (Alt 1987).

Tissue Differences in Metal Accumulation

Cadmium, iron, mercury, magnesium, manganese, selenium, and zinc accumulated differentially in tissues of northern pike and sheefish. The pattern of cadmium accumulation in northern pike, kidney>liver>muscle, agrees with that observed at the Kanuti Refuge (Mueller et al. 1995). Iron concentrations were significantly greater in kidney and liver than in muscle for northern pike and sheefish. These results differ from those of Mueller et al. (1993) and Snyder-Conn et al. (1992a,b) who reported that iron concentrations were highly variable among and within tissue types. Mercury concentrations of northern pike from our study were significantly greater in kidney and muscle than in liver. Similarly, mercury concentrations in muscle were significantly greater than in liver at the Kanuti Refuge (Mueller et al. 1995), but greater than in liver and kidney at the Nowitna Refuge (Snyder-Conn et al. 1992b).

Zinc concentrations in kidney were significantly greater than those in liver and muscle of northern pike and sheefish. A similar result occurred in longnose sucker (*Catostomus catostomus*) from the Kanuti Refuge. Zinc concentrations in kidney of northern pike from the Kanuti Refuge were also significantly greater than in muscle (Mueller et al. 1995). Miller et al. (1992) reported the rank of zinc in white sucker as liver> kidney> ovary/bone/testis> gill> muscle.

Trace Element Comparisons

The laboratory reported an LOD of 0.5 mg/kg for arsenic which is greater than baseline concentrations reported from other studies (Jenkins 1980; Wiener et al. 1981; Schmitt and Brumbaugh 1990; Snyder-Conn et al. 1992b; Mueller et al. 1993; Mueller et al. 1995). Twelve of 39 fish had at least one tissue sample with an arsenic concentration of 0.5 mg/kg or greater but, in general, arsenic concentrations were low; Moore and Ramamoorthy (1984) reported that in unpolluted or mildly contaminated waters, arsenic concentrations generally range from <0.4 - 1.6 mg/kg (assuming 75% moisture) . The Koyukuk Wilderness Area, downstream of the Hogatza River, on the Koyukuk River, has anomolously high arsenic values in sediment (Eppenger et al. 1994), but this did not result in high concentrations of arsenic in fish from the Hogatza River drainage.

Cadmium concentrations in tissue were low (Jenkins 1980, Wiener et al. 1981, Eisler 1985a, Schmitt and Brumbaugh 1990). Cadmium concentrations in kidney, liver, and muscle of northern pike were not significantly different from those measured at the Koyukuk (Snyder-Conn et al. 1992a), Nowitna (Snyder-Conn et al. 1992b), Kanuti (Mueller et al. 1995, except kidney), and Selawik refuges (Mueller et al. 1993).

The presence of mercury in fish tissue is widespread throughout the United States. EPA (1992) found mercury in fish tissue at 92% of 374 sites, most of which were contaminated, in the contiguous 48 states. However, the mean mercury concentration of EPA background sites was approximately 0.36 mg/kg dry weight (assuming 75% moisture). Similarly, the geometric mean mercury concentration of the U.S. Fish and Wildlife Service's National Contaminant Biomonitoring Program (NCBP) whole fish was 0.4 mg/kg (Schmitt and Brumbaugh 1990).

Mercury was detected in all fish regardless of location, except for the Alaska blackfish from Lower Camp Creek Adjacent. Mean concentrations of mercury in muscle samples were from 3.3 - 8.6 times greater than the mean background concentrations reported by EPA (1992) and for whole fish from the NCBP (Schmitt and Brumbaugh 1990). High concentrations of mercury in tissue can cause many types of abnormalities in fish; however, the central nervous system, i.e., the brain, is the probable site of the most harmful toxic action in fish exposed to mercury (Wiener and Spry 1996). In field studies and laboratory tests, mercury intoxication in fish has resulted in symptoms ranging from incoordination, diminished reponsiveness, reduced appetitie, and reduced growth to death (Wiener and Spry 1996). Bidwell and Heath (1993) concluded that rock bass (*Ambloplites rupestris*), in the South River, Virginia, were not adversely affected by mercury concentrations of 11.6 mg/kg (assuming 75% moisture) in liver and 5.6 mg/kg (assuming 75% moisture) in muscle. Based on the work of McKim et al. (1976), Wiener and Spry (1996) recommended that a concentration of 20 mg/kg (assuming 75% moisture) (5 mg/kg wet weight) be regarded as a no-observed-effect-concentration for salmonids. Based on these studies, fish within the Nowitna, Koyukuk, and Northern Innoko refuges are likely not suffering from reduced vigor as a result of mercury intoxication.

Mean mercury concentrations and ranges in northern pike muscle from each refuge of our study were greater than those reported for Kanuti (Mueller et al. 1995) and Selawik (Mueller et al. 1993) refuges. Snyder-Conn (1992b) reported a mean mercury concentration of 3.71 mg/kg in northern pike muscle from the Nowitna Refuge compared with 1.95 mg/kg from Sulatna and Sulukna river sites in the Nowitna Refuge from our study. Snyder-Conn et al. (1992b) found significantly greater concentrations of mercury in northern pike from the Sulukna River than from a site in the lower Nowitna River. They reported mercury concentrations from Sulukna River northern pike kidney ranging from 4.21 to 11.80 mg/kg. Mercury concentrations in tissue tend to increase with increased fish length but the mean fork length of northern pike in our study was greater than in Snyder-Conn et al. (1992b). The mean mercury concentration in sheefish kidney at the Sulukna River from our study was 4.38 mg/kg. The source of mercury in these fish has not been determined, but additional studies distinguishing the migratory habits of Nowitna River fish may help identify the source. Differing patterns of mercury accumulation in fish tissue has occurred among years. This may be due to the migratory habits of these fish or an indication of the variation of mercury concentrations in fish from the Nowitna Refuge.

In 1993, the mean concentration of mercury in 48 northern pike muscle samples from Kaiyuh Flats was 1.75 mg/kg (assuming 75% moisture) (Headlee 1996b) compared with 1.59 mg/kg

in our study. Whole juvenile Dolly Varden from Camp Creek downstream of the mine had a mean mercury concentration of 0.16 mg/kg, very low in comparison to other fish muscle samples and whole fish from the NCBP (Schmitt and Brumbaugh 1990); however, the other fish muscle and NCBP samples were composed of larger fish which tend to have greater concentrations of mercury.

Eight northern pike and four sheefish had at least one tissue with mercury concentrations greater than 4.0 mg/kg, the approximate dry weight equivalent of the Food and Drug Administration (FDA) 1.00 mg/kg wet weight action concentration for mercury. Mean mercury concentrations in kidney exceeded the FDA action concentration at the Sulukna River (sheefish) and the Hogatza River (northern pike). Mercury concentrations in kidney samples from northern pike at the Hogatza River ranged from 1.64 - 8.69 mg/kg ($\bar{x}$ = 6.34 mg/kg). Factors associated with the accumulation of high concentrations of mercury in fish include: piscivorous feeding habits, biomagnification of mercury in food chains, fish age and longevity, anthropogenic discharges of mercury to the environment, high water temperature, atmospheric deposition of mercury, and low acid-neutralizing capacity of surface waters (Wiener and Spry 1996). The fish and aquatic ecosystems of the Sulukna and Hogatza rivers could possess all of these factors except high water temperature. The acid-neutralizing capacity of the Hogatza River is particularly low (alkalinity = 17 mg/L), whereas that of the Sulukna River is moderate (alkalinity = 119 mg/L). Northern pike samples from the Hogatza River at the mouths of Clear and Caribou creeks were as indicative of the Hogatza River as of Clear and Caribou creeks because these fish likely inhabit both streams. There was no significant difference in mean mercury concentrations in tissue between these two Hogatza River sites.

Nearly all of the mercury in fish is methylmercury (Wiener and Spry 1996) and selenium has been shown to strongly bind with methylmercury (Sugiura et al. 1976; Eisler 1985b, 1987; Skorupa et al. 1996), providing an antagonistic (protective) effect. However, a synergistic (extra-toxic) seleniun-mercury interaction has been shown regarding reproductive impairment in mallard ducks (Heinz and Hoffman 1996). Selenium concentrations exceeded mercury concentrations in all kidney and liver samples of northern pike; however, mercury concentrations exceeded selenium concentrations in all northern pike muscle samples. In 1988 at the Kanuti Refuge, mean selenium concentrations in kidney, liver, and muscle of northern pike, longnose sucker, and Arctic grayling, always exceeded mercury concentrations (Mueller et al. 1995).

Selenium concentrations in northern pike kidney and muscle were significantly greater at the Koyukuk Refuge ($\bar{\times}$ = 1.70 mg/kg and 10.12 mg/kg, respectively) than at the Innoko ($\bar{\times}$ = 1.02 mg/kg and 6.91 mg/kg, respectively) and Nowitna ($\bar{\times}$ = 0.97 mg/kg and 6.15 mg/kg, respectively) refuges. The mean muscle concentration of selenium at the Koyukuk Refuge was far greater than the 0.72 mg/kg for whole northern pike from the NCBP. Snyder-Conn et al. (1992a) reported a mean of 1.15 mg/kg selenium in northern pike muscle from the Koyukuk Refuge. Headlee (1996b) measured <1.60 mg/kg (assuming 75% moisture) in muscle samples of 48 northern pike from Kaiyuh Flats in 1993. The mean selenium

concentrations in northern pike muscle and kidney from the Nowitna Refuge were comparable to those reported for the Nowitna Refuge by Snyder-Conn et al. (1992b). Mean selenium concentrations in northern pike kidney from all refuges in our study were greater than those from the Kanuti Refuge ($\bar{X}$ = 5.08 mg/kg); while mean selenium concentrations in northern pike muscle from the Nowitna and Northern Innoko refuges were less than those from the Kanuti Refuge (1.38 mg/kg) (Mueller et al. 1995). Mean selenium concentrations in northern pike muscle from the Koyukuk Refuge in our study were greater than those from the Kanuti Refuge.

Magnesium concentrations were greatest in muscle for northern pike and sheefish. Mean concentrations of magnesium in northern pike muscle from the three refuges in our study were similar to those reported for Koyukuk (Snyder-Conn et al. 1992a) and Kanuti (Mueller et al. 1995) refuges but are far less than those reported for the Nowitna Refuge (Snyder-Conn et al. 1992b). Manganese concentrations of northern pike at the Koyukuk Refuge were similar to those reported by Snyder-Conn et al. (1992a) from that refuge.

Zinc concentrations in northern pike kidney at the Northern Innoko Refuge were significantly greater than at Koyukuk and Nowitna refuges. Mean zinc concentrations of northern pike kidney samples from Koyukuk, Northern Innoko, and Nowitna refuges (613 mg/kg, 944 mg/kg, 413 mg/kg, respectively) were far greater than those reported for northern pike at the Kanuti Refuge (maximum mean concentration = 250 mg/kg) (Mueller et al. 1995). Mean zinc concentrations in northern pike kidney for Nowitna Refuge samples were the same as reported by Snyder-Conn (1992b). Mean concentrations of zinc in liver of northern pike were 156 mg/kg, 176 mg/kg, and 228 mg/kg for Koyukuk, Northern Innoko, and Nowitna refuges, respectively. Mean liver concentrations of zinc in 10 species of fish from the Great Lakes ranged from 44 to 192 mg/kg (Eisler 1993).

Mean zinc concentrations in northern pike muscle samples from Koyukuk, Northern Innoko, and Nowitna refuges were almost identical (20 mg/kg, 21 mg/kg, and 19 mg/kg, respectively) and similar to those from Kanuti (Mueller et al. 1995) and Koyukuk (Snyder-Conn 1992a) refuges. Snyder-Conn (1992b) reported zinc concentrations in northern pike muscle from Nowitna Refuge to be far greater than those measured in our study ($\bar{X}$ = 96.5 mg/kg). Zinc concentrations from our study are far less than the mean concentration in whole northern pike from two NCBP sites (314 mg/kg) (Schmitt and Brumbaugh 1990) and from muscle samples of several species of fish from the Great Lakes and rivers in the United States (Moore and Ramamoorthy 1984).

## CONCLUSIONS

Water quality characteristics of rivers sampled during this study are circumneutral in pH, calcium- and magnesium-bicarbonate based and typical of uncontaminated rivers.

Caribou Creek was very turbid due to placer mining in that drainage and Clear Creek was slightly turbid apparently due to natural causes. High concentrations of solids in water due to placer mining may be impacting fishery resources, including chum salmon spawning, at Caribou Creek. The inactive placer mine at Camp Creek apparently had little effect on water quality.

Concentrations of beryllium, cadmium, lead, and mercury in sediment samples were characteristic of uncontaminated sediments. Concentrations of copper, nickel, and zinc were significantly greater at Northern Innoko Refuge than from Koyukuk and Nowitna refuges. Copper and nickel concentrations in sediment appear to be high throughout interior Alaska. In general, samples from mined streams did not have greater concentrations of metals in sediments than those from unmined streams.

Arsenic and cadmium concentrations in fish tissue were low. Zinc concentrations were low in northern pike muscle but high in kidney from the Northern Innoko Refuge. Cadmium, iron, mercury, magnesium, manganese, selenium, and zinc accumulated differentially in tissues of northern pike and sheefish.

Mean concentrations of mercury in muscle samples were from 3.3 - 8.6 times greater than established mean background concentrations from other areas. Elevated mercury concentrations in fish may result in concentration of mercury in piscivores. Selenium concentrations in northern pike muscle also were greater than established mean background concentrations from other areas. Selenium concentrations exceeded mercury concentrations in kidney and liver but not muscle of northern pike.

## RECOMMENDATIONS

The watersheds of Clear and Caribou creeks should be monitored on a regular basis to determine the impacts on fish, water, and sediment quality due to placer mining. The emphasis should be on protection of summer chum salmon spawning habitat.

The source of high mercury concentrations in fish from the Hogatza and Sulukna rivers should be determined. Towards this goal, studies distinguishing the migratory habits of fish, including delineation of overwintering areas, from these drainages should be conducted.

Gill histopathology should be performed on northern pike and sheefish from potentially development-impacted streams to establish a baseline. Gill tissue is comparitively fragile and is readily impacted by contaminants, including metals. Monitoring gill tissue for contaminant impacts is relatively inexpensive and thus may serve as a good method for monitoring impacted waterbodies.

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## APPENDIX A: DOCUMENTATION AND SAMPLE HANDLING

### STUDY PROPOSALS

A study proposal was submitted prior to each year of sampling. 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.

### FIELD DOCUMENTATION

During field studies, sample documentation was recorded in a waterproof field notebook in permanent ink. The date and time of collections at each site were specified as were the 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 or tissue weights (as 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 quality, 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 samples), the sample location, sample weight or volume, and analyses requested for each particular sample. The catalogs were submitted to the following analytical laboratories:

| Catalog | Regional I.D. | Laboratory Address |
|---|---|---|
| 7030006 | R7105-1261 | Geochemical and Environmental Research Group<br>Texas A&M University<br>833 Graham Road<br>College Station, TX 77845 |
| 7030003 | R7105-1261 | Research Triangle Institute (RTI)<br>Cornwallis Road<br>P.O. Box 12194<br>Research Triangle Park, NC 27709 |

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.

## CHAIN OF CUSTODY

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

## SAMPLE STORAGE AND SHIPMENT

Sediment and fish samples were placed in coolers with blue ice and transported by float plane to freezers for storage. Samples were shipped to the laboratory by air courier. Frozen samples were shipped with dry ice.

## SAMPLE HOLDING TIMES

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.

## APPENDIX B: SAMPLE IDENTIFICATION AND DATA BASE MANAGEMENT

Field sample numbers were transformed into identification numbers consistent with the Fairbanks Ecological Services' Contaminants Data Base Management System. Sample data were entered into this system, as follows:

CONTAMINANTS DATABASE ENTRY FIELDS

Sample Identification Database Fields:

| FIELD NAME | FIELD DESCRIPTION | EXAMPLE | ENTRY DESCRIPTION | COMMENT |
|---|---|---|---|---|
| ID | Sample ID # | 88AA501ARK | A composite of next 6 fields | |
| 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 | Sequential letters |
| S | Species code or type of sample | B | Burbot | 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* | | 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 submitted sample | |
| 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 | Default is ppm |
| 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] |
| X and the metal symbol | Less than for each metal | < | Less than | 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 a year (e.g., for first sample date at a site, N = 1, the next sample period at the site within the same year, N = 2, etc.).

[2] Overflow is to be used when necessary to form a unique ID when all other fields are the same for two samples, 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, laboratorys vary in how other matrices are reported.

General Location Codes

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

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
I - chum salmon
H - chinook 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
Q - king eider
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 - hair
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 ($H_2O$)
U - shoots
V - leaves
W - whole (tissue or sediment)
Z - stem

## APPENDIX C: QUALITY ASSURANCE/QUALITY CONTROL 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.

Contract laboratories are selected by a PACF technical committee using a process involving the correct analysis of samples submitted to prospective laboratories by PACF, and a review of the laboratory, its procedures, facilities, experience, and personnel. A final step in selecting a laboratory is an on-site inspection by representatives of the evaluation committee. Continued round-robin testing and cross-checking of contract laboratories by PACF has been used to monitor their 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 to contract laboratories are also reanalyzed by PACF. 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. Reports produced by contract laboratories are 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, and the specific instrumentation used, including model numbers.

QA-QC data produced during this study were analyzed using a computer program, written by Patrick Scannell, Ecological Services, Fairbanks, designed to screen QA-QC data. Variables and screening criteria utilized in this software are presented below.

## LIMITS OF DETECTION

The criterion "limit of detection" (LOD) has been variously defined and its determination is the subject of controversy (Greenberg et al. 1992). 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 consistently detectable and distinguishable from instrument noise. Samples reported as being below the detection limit in a data set are reported as <X where X is the LOD.

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. 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 LOD for QA-QC screening of the data.

## ANALYTICAL PRECISION

Precision refers to the degree of agreement among repeated measurements of a given sample. 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 used for this study were made using duplicate analysis, where at least two subsamples of a homogenized sample are collected and analyzed by the contract laboratory. Precision is monitored by the contract laboratory using range ratio control charts for each analyte of each matrix (sediment, tissue). The measure selected for estimating precision by the QA-QC analysis program 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 determined by the first analysis, and $D_2$ is the concentration as determined by the second analysis.

Acceptable precision is based not only on the absolute value of the RPD, but also on the relationship between the concentration of the analyte and the LOD for that analyte. For duplicate samples with analyte concentrations where both values are less than the LOD, no estimate of precision is made in the screening software, because this comparison is normally inappropriate (Greenberg et al. 1992). When one duplicate value is less than the LOD and the other greater than the LOD, an RPD is calculated by assuming that the number less than the LOD equals the LOD. For sample concentrations less than twice the LOD, precision is expected to be low, because instrument performance typically declines as the LOD is approached. The 95% confidence interval for these cases is assumed to be 2(LOD) (or up to 200% of the actual reported value of a single sample). Samples with concentrations less than 2(LOD) are not rejected, based on poor precision; however, these data are flagged as "qualitative only" by the screening program.

Because the LOD may vary according to sample, the LOD used in the QA-QC screening program is the highest LOD identified for each sample matrix in the 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 expected to be semi-quantitative, and dependent on their relation to the LOD. In these samples, both precision and accuracy may be reduced. For measurements >10(LOD), analyses can be expected to be highly quantitative. However, the same criterion, ±20%, is applied for screening data values both between >2(LOD) and <10(LOD), and >10(LOD). The QA-QC 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.

## ANALYTICAL ACCURACY

### *Spiked Samples*

In addition to precision, measurements of correctness of the analyses are needed to guarantee the quality of semi-quantitative (>2<10 LOD) and quantitative (>10 LOD) data, and to estimate chemical interferences that may occur. One method used by Service contract laboratories to estimate accuracy and gauge interference is the use of spiked samples. This method consists of dividing a homogenized sample into two subsamples, analyzing one as the sample, spiking the other subsample with a known quantity of one or more analytes, and analyzing the resulting mixture. 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, or that contamination of the sample may have occurred. Recoveries of less than 100% could occur due to loss of the analyte during the sample procedure (e.g., loss of mercury due to volatility), instrument drift downward, errors in the calibration procedure, or chemical interferences inherent in the matrix being analyzed.

Another important reason for imprecise metal recoveries is incomplete digestion of the sample material. Unless specified in the catalog instructions, metal digestions performed on sediment samples 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 nitric and 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). The QA-QC screening computer program used for this study examines spike recoveries for all spiked samples, even if the spike was low.

In general, Service contract laboratories perform incomplete digestions with nitric and perchloric acids; 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 because contaminants could remain bound to materials in media, and thus be unavailable for biogeochemical cycling.

The spike recovery criteria adopted for the computer program, 80-120% average recovery, are based on Service criteria presented by Moore (1990) and Greenberg et al. (1992). The program identifies all analytes for which the average spike recovery (average of all spikes for that analyte and matrix) fail this test. These criteria are as stringent or more stringent than the Greenberg et al. (1992) criteria for performance evaluation samples of water and wastewater.

*Standard Reference Materials*

Standard reference materials (SRM's) or interim reference materials provided by an outside agency or commercial source, represent an additional means of gauging the accuracy of 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 included the National Institute of Standards and Technology (formerly the National Bureau of Standards), and the National Research Council of Canada (NRCC). 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 the source of the analyte. In some cases, a considerable amount of professional judgement is used to define this range.

Some analyte values may be 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 National Institute of Standards and Technology 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 less than 2(LOD), because this comparison would be qualitative only. The QA-QC Summary Sheet, produced by the screening program, lists "Ref. Val. < LOD" for these cases. The following screening criteria were used to evaluate the accuracy of SRM analyses for which measured values were greater than 2 LOD.

When the certified values are greater than 2(LOD) and the mean value of an analyte as measured by the laboratory is within ± 20% of the certified value, the SRM data are considered acceptable. The QA-QC computer program does not use this method of comparison so these comparisons were calculated manually.

This screening method results in acceptance or rejection of SRM performance comparable to that of the National Status and Trends Program which relies on acceptance of all values within ± 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) ± 20%.

*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.

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 for sediment and tissue samples, and when a reagent blank analysis indicates contamination. A reagent blank is distilled and deionized water that is passed through the analytical procedure with the other samples. Reagent blanks are subjected to the same digestion procedures as samples. 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.

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 blank values may be subtracted from the data set. Blank samples used in quality control for sample catalogs are summarized in Appendix D.

The QA-QC computer program examines blank contamination in relation to concentrations of each analyte detected in the duplicate analyses (presumably selected at random 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 LOD, this percent is reported, and the data are rejected.

**APPENDIX D: QUALITY ASSURANCE QUALITY CONTROL SCREENING RESULTS**

Catalog 7030006

Koyukuk/Nowitna/N. Innoko NWR - Fish 1991

Acceptable Data

| Analyte | Method | Mean RPD[1] | Precision[2] | Mean Spike[3] | Mean SRM[4] | Blank[5] |
|---|---|---|---|---|---|---|
| Arsenic | AA | 15.6 | Qualitative | 114.2 | 100 | 0 |
| Boron | ICP | 0.0 | Quantitative | 95.1 | NRV | 0 |
| Beryllium | ICP | 3.5 | Quantitative | 104.9 | NRV | 0 |
| Cadmium | AA | 5.2 | Quantitative | 82.0 | 103 | 0 |
| Iron | ICP | 9.3 | Quantitative | 119.3 | 109 | 0 |
| Lead | AA | 0.0 | Qualitative | 99.1 | 116 | 0 |
| Magnesium | ICP | 11.5 | Quantitative | 108.4 | 90 | 0 |
| Manganese | ICP | | Quantitative | None | 111 | 0 |
| Mercury | AA | 11.8 | Quantitative | 97.5 | 84 | 0 |
| Selenium | AA | 5.1 | Quantitative | 111.0 | 102 | 0 |
| Zinc | ICP | 4.3 | Quantitative | 115.0 | 99 | 0 |

Catalog 7030006
Koyukuk/Nowitna/N. Innoko NWR - Fish 1991
Questionable Data

| Analyte | Method | Mean RPD[1] | Mean Spike[3] | Mean SRM[4] | Blank[5] |
|---|---|---|---|---|---|
| Aluminum[6] | ICP | | | | |
| Chromium | ICP | 28.5 | 100.1 | 99 | 0 |
| Copper | ICP | 21.5 | 111.7 | 89 | 1.39 |
| Molybdenum | ICP | 59.0 | 99.2 | NRV | 0 |
| Nickel | ICP | 150.0 | 114 | 201 | 0 |
| Strontium | ICP | 0 | 81.8 | NRV | 0 |
| Vanadium | ICP | 42.2 | 95.5 | NRV | 2.42 |

[1] The average relative percent difference (RPD) from duplicate sample analyses, indicating precision.

[2] When either duplcate analysis had a value less than twice the LOD, the precision could not be estimated and the corresponding data are considered qualitative.

[3] The average percent spike recovery. Average spike recoveries <80% or >120% are considered unacceptable.

[4] The percent deviation of the mean SRM analysis result from the certified mean value. Deviations >± 20% are unacceptable. NRV means that no relevant SRM value was available.

[5] The highest concentration of an analyte found in a method blank treated as a sample by the laboratory. Blanks >15% of the LOD are unacceptable.

[6] The analytical laboratory reported that aluminum data were not acceptable.

Catalog 7030003
Koyukuk/Nowitna/N. Innoko NWR - Sediment 1991
Acceptable Data

| Analyte | Method | Mean RPD[1] | Precision[2] | Mean Spike[3] | Mean SRM[4] | Blank[5] |
|---|---|---|---|---|---|---|
| Boron | ICP | 10.2 | Qualitative | 834 | NRV | 0 |
| Beryllium | ICP | 13.5 | Quantitative | 105 | NRV | 0 |
| Cadmium | ICP | 14.1 | Quantitative | 102 | 96 | 0 |
| Copper | ICP | 2.2 | Quantitative | 106 | 99 | 0 |
| Lead | ICP | 6.0 | Quantitative | 101 | 102 | 0 |
| Manganese | ICP | 1.5 | Quantitative | 87 | NRV | 0 |
| Mercury | AA | 0.0 | Qualitative | 91 | 91 | 0 |
| Molybdenum | ICP | 0.0 | Qualitative | 88 | NRV | 0 |
| Nickel | ICP | 7.3 | Quantitative | 103 | 91 | 0 |
| Strontium | ICP | 9.6 | Quantitative | 105 | NRV | 0 |
| Zinc | ICP | 5.3 | Quantitative | 100 | 94 | 0 |

Catalog 7030003
Koyukuk/Nowitna/N. Innoko NWR - Sediment 1991
Questionable Data

| Analyte | Method | Mean RPD[1] | Mean Spike[3] | Mean SRM[4] | Blank[5] |
|---|---|---|---|---|---|
| Aluminum | ICP | 14.5 | 82.7 | 21 | 0 |
| Barium | ICP | 3.1 | 102.7 | 19 | 0 |
| Chromium | ICP | 7.9 | 101.3 | 61 | 0 |
| Iron | ICP | 4.4 | 99.1 | 77 | 0 |
| Magnesium | ICP | 7.3 | 88.5 | 72 | 0 |
| Vanadium | ICP | 11.3 | 103.4 | 19 | 0 |

[1] The average relative percent difference (RPD) from duplicate sample analyses, indicating precision.

[2] When either duplcate analysis had a value less than twice the LOD, the precision could not be estimated and the corresponding data are considered qualitative.

[3] The average percent spike recovery. Average spike recoveries <80% or >120% are considered unacceptable.

[4] The percent deviation of the mean SRM analysis result from the certified mean value. Deviations >± 20% are unacceptable. NRV means that no relevant SRM value was available.

[5] The highest concentration of an analyte found in a method blank treated as a sample by the laboratory. Blanks >15% of the LOD are unacceptable.

**APPENDIX E: METALS CONCENTRATIONS IN SEDIMENT FROM KOYUKUK, NORTHERN UNIT OF INNOKO, AND NOWITNA NATIONAL WILDLIFE REFUGES, ALASKA 1991.**

| | | Metals Concentrations (mg/kg dry weight) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Site | Rep. | Be | B | Cd | Cu | Pb | Mn | Hg | Mo | Ni | Sr | Zn |
| KY4 | A | 0.47 | <5.00 | 0.41 | 27.8 | 18.7 | 487 | <0.14 | <5.00 | 32.7 | 28.9 | 79.0 |
| KY4 | B | 1.10 | <5.00 | 1.06 | 30.5 | 25.4 | 597 | <0.14 | <5.00 | 36.8 | 25.1 | 86.4 |
| KY4 | C | 8.83 | 13.20 | 8.13 | 34.8 | 57.4 | 530 | <0.14 | 8.36 | 68.1 | 33.4 | 81.4 |
| KY6 | A | 0.51 | <5.00 | 0.47 | 24.4 | 8.6 | 464 | <0.14 | <5.00 | 29.6 | 22.9 | 67.4 |
| KY6 | B | 0.40 | <5.00 | <0.20 | 24.5 | 11.1 | 457 | <0.14 | <5.00 | 29.6 | 22.8 | 72.5 |
| KY6 | C | 1.54 | 7.31 | 1.30 | 26.3 | 16.8 | 487 | <0.14 | <5.00 | 33.6 | 21.9 | 64.3 |
| IN11 | A | 0.58 | 11.30 | 0.92 | 41.1 | 15.9 | 640 | <0.14 | <5.00 | 40.5 | 33.3 | 95.2 |
| IN11 | B | 0.32 | 7.39 | 0.72 | 35.5 | 18.8 | 743 | <0.14 | <5.00 | 36.4 | 31.6 | 82.3 |
| IN11 | C | 0.95 | 6.81 | 1.12 | 36.1 | 15.1 | 646 | <0.14 | <5.00 | 38.8 | 32.3 | 81.8 |
| IN12 | A | 0.22 | <5.00 | 0.38 | 39.0 | 25.7 | 1500 | <0.14 | <5.00 | 61.8 | 21.2 | 89.4 |
| IN12 | B | 0.48 | 5.97 | 0.52 | 25.1 | 7.0 | 244 | <0.14 | <5.00 | 33.1 | 21.4 | 62.6 |
| IN12 | C | <0.20 | <5.00 | 0.30 | 28.7 | 12.1 | 591 | <0.14 | <5.00 | 45.7 | 15.4 | 68.3 |
| IN13 | A | <0.20 | <5.00 | 1.00 | 36.0 | 12.7 | 1350 | <0.14 | <5.00 | 86.0 | 11.6 | 103.0 |
| IN13 | B | <0.20 | <5.00 | 0.73 | 37.7 | 15.1 | 1000 | <0.14 | <5.00 | 79.0 | 11.8 | 111.0 |
| IN13 | C | <0.20 | <5.00 | <0.20 | 32.5 | 8.3 | 941 | <0.14 | <5.00 | 69.7 | 12.0 | 101.0 |

Appendix E. cont.

| Site | Rep. | Be | B | Cd | Cu | Pb | Mn | Hg | Mo | Ni | Sr | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| IN14 | A | 0.42 | <5.00 | 0.37 | 41.9 | 13.4 | 541 | <0.14 | <5.00 | 40.8 | 28.1 | 132.0 |
| IN14 | B | 0.62 | 7.73 | 0.83 | 38.7 | 12.6 | 387 | <0.14 | <5.00 | 42.1 | 27.0 | 123.0 |
| IN14 | C | 0.45 | <5.00 | 0.67 | 40.6 | 14.3 | 452 | <0.14 | <5.00 | 42.4 | 27.2 | 133.0 |
| IN16 | A | 0.41 | <5.00 | 0.40 | 32.3 | 17.0 | 590 | <0.14 | <5.00 | 34.3 | 29.6 | 90.0 |
| IN16 | B | 0.60 | 7.96 | 0.79 | 33.6 | 13.5 | 576 | <0.14 | <5.00 | 41.4 | 30.9 | 105.0 |
| IN16 | C | 0.37 | 5.50 | <0.20 | 29.4 | 13.0 | 547 | <0.14 | <5.00 | 36.1 | 31.3 | 92.2 |
| IN17 | A | 0.49 | <5.00 | 0.53 | 39.3 | 13.6 | 333 | <0.14 | <5.00 | 40.1 | 31.9 | 118.0 |
| IN17 | B | 0.52 | 9.11 | 0.40 | 40.8 | 10.5 | 698 | <0.14 | <5.00 | 40.0 | 40.9 | 92.1 |
| IN17 | C | 0.51 | 5.29 | 0.80 | 43.4 | 11.4 | 508 | <0.14 | <5.00 | 43.3 | 34.9 | 107.0 |
| NO2 | A | 0.31 | <5.00 | <0.20 | 25.2 | 12.6 | 511 | <0.14 | <5.00 | 31.1 | 26.6 | 81.5 |
| NO2 | B | 0.33 | <5.00 | 0.27 | 28.1 | 9.4 | 620 | <0.14 | <5.00 | 27.0 | 24.5 | 77.8 |
| NO2 | C | 0.33 | <5.00 | 0.29 | 28.4 | 8.8 | 709 | <0.14 | <5.00 | 29.2 | 27.5 | 83.0 |
| NO4 | A | 0.30 | 6.95 | 0.27 | 14.8 | 7.8 | 378 | <0.14 | <5.00 | 23.1 | 49.9 | 53.7 |
| NO4 | B | 0.32 | <5.00 | 0.22 | 25.8 | 11.5 | 550 | <0.14 | <5.00 | 28.1 | 53.8 | 67.1 |
| NO4 | C | 0.25 | <5.00 | <0.20 | 17.2 | 10.2 | 436 | <0.14 | <5.00 | 24.4 | 57.1 | 61.3 |
| NO6 | A | 0.45 | <5.00 | 0.32 | 37.2 | 12.9 | 253 | <0.14 | <5.00 | 32.4 | 19.1 | 105.0 |
| NO6 | B | 0.41 | 6.00 | 0.30 | 27.9 | 10.3 | 200 | <0.14 | <5.00 | 28.4 | 17.7 | 103.0 |
| NO6 | C | 0.60 | <5.00 | 0.72 | 42.0 | 20.4 | 307 | <0.14 | <5.00 | 39.6 | 26.6 | 158.0 |

Appendix E. cont.

| Site | Rep. | Be | B | Cd | Cu | Pb | Mn | Hg | Mo | Ni | Sr | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NO7 | A | 0.31 | <5.00 | <0.20 | 24.4 | 12.2 | 707 | <0.14 | <5.00 | 27.0 | 60.8 | 73.9 |
| NO7 | B | 0.29 | <5.00 | <0.20 | 24.0 | 11.5 | 667 | <0.14 | <5.00 | 26.4 | 56.4 | 71.2 |
| NO7 | C | 0.34 | <5.00 | <0.20 | 25.6 | 12.5 | 643 | <0.14 | <5.00 | 28.5 | 58.8 | 75.9 |

**APPENDIX F: METALS CONCENTRATIONS OF KIDNEY, LIVER, MUSCLE AND WHOLE BODY, AND TOTAL LENGTH, FORK LENGTH AND WEIGHT OF ALASKA BLACKFISH (*DALLIA PECTORALIS*), ARCTIC GRAYLING (*THYMALLUS ARCTICUS*), AND NORTHERN PIKE (*ESOX LUCIUS*), COLLECTED FROM KOYUKUK AND NORTHERN INNOKO NATIONAL WILDIFE REFUGES, ALASKA, 1991. Total and fork lengths, and weight are expressed as mm and kg, respectively.**

| | | | | | | | Metals Concentrtions (mg/kg dry weight) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Site | Species[a] | Tissue | Date | T.L. | F.L. | Wt. | As | B | Be | Cd | Fe | Pb | Hg | Mg | Mn | Se | Zn |
| KY4 | AG | K | 18 Jun | 390 | 364 | 0.55 | [b] | | | | | | 0.76 | | | | |
| KY4 | AG | L | 18 Jun | 390 | 364 | 0.55 | | | | | | | 0.43 | | | | |
| KY4 | AG | M | 18 Jun | 390 | 364 | 0.55 | <0.05 | <2.00 | <0.10 | <0.10 | 52 | <0.50 | 0.56 | 947 | <1.00 | 1.75 | 18 |
| KY4 | NP | K | 18 Jun | 618 | 585 | 1.45 | <0.05 | <2.00 | 0.24 | 0.36 | 280 | <0.50 | 4.00 | 677 | 1.89 | 9.65 | 560 |
| KY4 | NP | L | 18 Jun | 618 | 585 | 1.45 | <0.05 | <2.00 | 0.29 | <0.10 | 534 | <0.50 | 1.36 | 263 | 2.78 | 4.89 | 94 |
| KY4 | NP | M | 18 Jun | 618 | 585 | 1.45 | <0.05 | <2.00 | 0.39 | <0.10 | <5 | <0.50 | 3.01 | 873 | 5.73 | 1.56 | 17 |
| KY4 | NP | K | 18 Jun | 742 | 698 | 2.30 | <0.05 | <2.00 | <0.10 | 0.28 | 263 | <0.50 | 2.96 | 645 | <1.00 | 8.58 | 689 |
| KY4 | NP | L | 18 Jun | 742 | 698 | 2.30 | <0.05 | <2.00 | <0.10 | 0.27 | 381 | <0.50 | 1.51 | 551 | 5.07 | 6.75 | 145 |
| KY4 | NP | M | 18 Jun | 742 | 698 | 2.30 | <0.05 | <2.00 | <0.10 | <0.10 | 19 | <0.50 | 2.86 | 1257 | 1.81 | 1.58 | 21 |
| KY4 | NP | K | 18 Jun | 643 | 602 | 1.65 | <0.05 | 3.44 | <0.10 | 0.62 | 324 | <0.50 | 2.65 | 684 | <1.00 | 9.76 | 570 |
| KY4 | NP | L | 18 Jun | 643 | 602 | 1.65 | <0.05 | <2.00 | <0.10 | 0.14 | 1350 | <0.50 | 0.97 | 437 | 4.85 | 5.51 | 148 |
| KY4 | NP | M | 18 Jun | 643 | 602 | 1.65 | <0.05 | <2.00 | <0.10 | <0.10 | 40 | <0.50 | 2.19 | 1310 | 4.29 | 1.66 | 18 |
| KY4 | NP | K | 18 Jun | 631 | 602 | 1.45 | <0.05 | <2.00 | 0.43 | 0.63 | 441 | <0.50 | | 590 | 6.83 | 13.20 | 530 |
| KY4 | NP | L | 18 Jun | 631 | 602 | 1.45 | <0.05 | <2.00 | 0.29 | 0.18 | 2210 | <0.50 | 3.96 | 425 | 7.36 | 8.89 | 146 |
| KY4 | NP | M | 18 Jun | 631 | 602 | 1.45 | <0.05 | <2.00 | <0.10 | <0.10 | 67.8 | <0.50 | 6.36 | 1298 | 8.03 | 1.71 | 18 |
| KY6 | NP | K | 19 Jun | | | | <0.05 | <2.00 | <0.10 | 0.33 | 293 | <0.50 | 7.83 | 654 | 3.68 | 10.60 | 326 |

Appendix F Cont.

| Site | Species | Tissue | Date | T.L. | F.L. | Wt. | As | B | Be | Cd | Fe | Pb | Hg | Mg | Mn | Se | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KY6 | NP | L | 19 Jun | | | | <0.05 | <2.00 | <0.10 | 0.14 | 850 | <0.50 | 2.83 | 432 | 4.61 | 5.80 | 82 |
| KY6 | NP | M | 19 Jun | | | | <0.05 | <2.00 | <0.10 | <0.10 | 15 | <0.50 | 3.80 | 1172 | 2.42 | 2.18 | 18 |
| KY6 | NP | K | 19 Jun | | | | <0.05 | <2.00 | 0.12 | 0.34 | 318 | <0.50 | 4.19 | 743 | 2.27 | 9.35 | 605 |
| KY6 | NP | L | 19 Jun | | | | <0.05 | <2.00 | 0.10 | 0.11 | 975 | <0.50 | 2.60 | 438 | 4.51 | 5.98 | 113 |
| KY6 | NP | M | 19 Jun | | | | <0.05 | <2.00 | <0.10 | <0.10 | 29 | <0.50 | 1.92 | 1194 | <1.00 | 1.76 | 21 |
| KY6 | NP | K | 19 Jun | | | | <0.05 | <2.00 | <0.10 | 0.38 | 291 | <0.50 | 1.64 | 753 | 5.12 | 9.30 | 936 |
| KY6 | NP | L | 19 Jun | | | | <0.05 | <2.00 | <0.10 | <0.10 | 1060 | <0.50 | 0.79 | 567 | 5.72 | 5.47 | 153 |
| KY6 | NP | M | 19 Jun | | | | <0.05 | <2.00 | <0.10 | <0.10 | 46 | <0.50 | 1.90 | 2985 | <1.00 | 1.57 | 20 |
| KY6 | NP | K | 19 Jun | 628 | 588 | 1.50 | <0.05 | <2.00 | <0.10 | 0.61 | 352 | <0.50 | 3.00 | 699 | 1.16 | 9.80 | 449 |
| KY6 | NP | L | 19 Jun | 628 | 588 | 1.50 | <0.05 | <2.00 | <0.10 | 0.15 | 1020 | <0.50 | 1.86 | 567 | 5.66 | 6.68 | 119 |
| KY6 | NP | M | 19 Jun | 628 | 588 | 1.50 | <0.05 | <2.00 | <0.10 | <0.10 | 18 | <0.50 | 3.47 | 1100 | 3.23 | 1.56 | 23 |
| KY6 | NP | K | 19 Jun | 973 | 968 | 4.60 | <0.05 | <2.00 | 0.33 | 0.56 | 387 | <0.50 | 8.69 | 747 | 6.22 | 10.80 | 850 |
| KY6 | NP | L | 19 Jun | 973 | 968 | 4.60 | <0.05 | <2.00 | <0.10 | 0.28 | 612 | <0.50 | 7.73 | 450 | 3.13 | 11.50 | 406 |
| KY6 | NP | M | 19 Jun | 973 | 968 | 4.60 | 8.1 | <2.00 | <0.10 | <0.10 | 35 | <0.50 | 6.15 | 1047 | <1.00 | 1.61 | 22 |
| IN11 | AB | W | 13 Jun | | | | <0.05 | <2.00 | <0.10 | <0.10 | 413 | <0.50 | <0.10 | 1500 | 22.80 | 1.32 | 273 |
| IN12 | DV | W | 12 Jun | | | | <0.05 | <2.00 | 1.24 | 0.36 | 347 | <0.50 | 0.18 | 816 | 20.60 | 6.68 | 122 |
| IN12 | DV | W | 12 Jun | | | | <0.05 | <2.00 | 1.42 | 0.38 | 307 | 0.98 | 0.15 | 741 | 15.60 | 5.53 | 120 |
| IN12 | DV | W | 12 Jun | | | | <0.05 | <2.00 | 1.86 | 0.32 | 244 | <0.50 | 0.15 | 683 | 12.40 | 5.67 | 116 |
| IN14 | NP | K | 13 Jun | 614 | 583 | 1.50 | | | | | | | 0.89 | | | | |
| IN14 | NP | L | 13 Jun | 614 | 583 | 1.50 | <0.05 | <2.00 | 0.51 | <0.10 | 611 | <0.50 | 0.27 | 384 | 1.48 | 3.74 | 145 |
| IN14 | NP | M | 13 Jun | 614 | 583 | 1.50 | 0.7 | <2.00 | <0.10 | <0.10 | 22 | <0.50 | 1.48 | 1530 | <1.00 | 0.63 | 27 |
| IN14 | NP | K | 13 Jun | 576 | 547 | 1.10 | | | | | | | 0.77 | | | | |

Appendix F Cont.

| Site | Species | Tissue | Date | T.L. | F.L. | Wt. | As | B | Be | Cd | Fe | Pb | Hg | Mg | Mn | Se | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| IN14 | NP | L | 13 Jun | 576 | 547 | 1.10 | <0.05 | <2.00 | <0.10 | 0.10 | 882 | <0.50 | 0.42 | 561 | 6.11 | 4.97 | 145 |
| IN14 | NP | M | 13 Jun | 576 | 547 | 1.10 | <0.05 | 3.33 | <0.10 | <0.10 | 8 | <0.50 | 1.46 | 1047 | 5.30 | 1.18 | 19 |
| IN14 | NP | K | 13 Aug | 770 | 700 | | <0.05 | <2.00 | <0.10 | <0.10 | 408 | <0.50 | 1.66 | 5 | 1.00 | 6.84 | 937 |
| IN14 | NP | L | 13 Aug | 770 | 700 | | <0.05 | <2.00 | <0.10 | 0.12 | 300 | <0.50 | 0.72 | 440 | 4.55 | 5.12 | 137 |
| IN14 | NP | M | 13 Aug | 770 | 700 | | <0.05 | <2.00 | 0.45 | 0.34 | 27 | <0.50 | 2.04 | 993 | 4.66 | 1.03 | 17 |
| IN14 | NP | K | 13 Aug | 685 | 650 | | | | | | | | 1.35 | | | | |
| IN14 | NP | L | 13 Aug | 685 | 650 | | <0.05 | <2.00 | <0.10 | 0.29 | 1960 | <0.50 | 0.99 | 518 | 7.35 | 8.10 | 253 |
| IN14 | NP | M | 13 Aug | 685 | 650 | | <0.05 | <2.00 | 0.32 | 0.36 | <5 | <0.50 | 2.25 | 1358 | 6.59 | 1.60 | 16 |
| IN14 | NP | K | 13 Aug | 585 | 555 | | <0.05 | <2.00 | 0.44 | 0.52 | 550 | <0.50 | 0.90 | 801 | 6.28 | 6.30 | 766 |
| IN14 | NP | L | 13 Aug | 585 | 555 | | <0.05 | <2.00 | 0.30 | 0.13 | 798 | <0.50 | 0.51 | 401 | 5.67 | 7.37 | 201 |
| IN14 | NP | M | 13 Aug | 585 | 555 | | 0.6 | <2.00 | <0.10 | 0.27 | 30 | <0.50 | 1.39 | 1161 | <1.00 | 1.39 | 17 |
| IN16 | NP | K | 30 Aug | 570 | 550 | 1.20 | | | | | | | 0.59 | | | | |
| IN16 | NP | L | 30 Aug | 570 | 550 | 1.20 | <0.05 | <2.00 | <0.10 | <0.10 | 476 | <0.50 | 0.15 | 465 | 3.14 | 5.88 | 154 |
| IN16 | NP | M | 30 Aug | 570 | 550 | 1.20 | <0.05 | <2.00 | 0.34 | <0.10 | 51 | <0.50 | 0.82 | 1328 | 5.30 | 1.08 | 19 |
| IN16 | NP | K | 30 Aug | 690 | 650 | 1.90 | <0.05 | <2.00 | <0.10 | 0.45 | 748 | <0.50 | 0.36 | 725 | 2.29 | 9.10 | 1150 |
| IN16 | NP | L | 30 Aug | 690 | 650 | 1.90 | <0.05 | <2.00 | 0.22 | <0.10 | 1360 | <0.50 | 0.68 | 240 | 3.70 | 10.00 | 184 |
| IN16 | NP | M | 30 Aug | 690 | 650 | 1.90 | <0.05 | <2.00 | <0.10 | <0.10 | 41 | <0.50 | 1.81 | 1290 | <1.00 | 1.10 | 34 |
| IN16 | NP | K | 30 Aug | 795 | 760 | 2.80 | <0.05 | <2.00 | 0.36 | 0.47 | 468 | <0.50 | 3.09 | 689 | 5.63 | 8.50 | 1030 |
| IN16 | NP | L | 30 Aug | 795 | 760 | 2.80 | <0.05 | <2.00 | <0.10 | 0.11 | 343 | <0.50 | 1.11 | 468 | 2.34 | 5.94 | 260 |
| IN16 | NP | M | 30 Aug | 795 | 760 | 2.80 | <0.05 | <2.00 | <0.10 | <0.10 | 51 | <0.50 | 2.07 | 1292 | <1.00 | 1.08 | 25 |
| IN16 | NP | K | 30 Aug | 910 | 865 | 5.10 | <0.05 | <2.00 | 0.34 | 0.34 | 448 | <0.50 | 2.62 | 630 | 4.45 | 5.30 | 1050 |
| IN16 | NP | L | 30 Aug | 910 | 865 | 5.10 | <0.05 | <2.00 | <0.10 | <0.10 | 107 | 0.52 | 1.02 | 683 | 2.06 | 5.44 | 113 |
| IN16 | NP | M | 30 Aug | 910 | 865 | 5.10 | <0.05 | <2.00 | <0.10 | <0.10 | 59 | <0.50 | 2.02 | 1274 | <1.00 | 0.85 | 17 |

Appendix F Cont.

| Site | Species | Tissue | Date | T.L. | F.L. | Wt. | As | B | Be | Cd | Fe | Pb | Hg | Mg | Mn | Se | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| IN16 | NP | K | 30 Aug | 695 | 665 | 2.10 | <0.05 | <2.00 | <0.10 | 0.24 | 373 | <0.50 | 0.90 | 693 | <1.00 | 5.30 | 840 |
| IN16 | NP | L | 30 Aug | 695 | 665 | 2.10 | <0.05 | <2.00 | <0.10 | <0.10 | 332 | <0.50 | 0.42 | 524 | 4.73 | 4.38 | 147 |
| IN16 | NP | M | 30 Aug | 695 | 665 | 2.10 | | <2.00 | <0.10 | <0.10 | | <0.50 | 1.47 | 1089 | 3.22 | 1.10 | 23 |
| IN17 | NP | K | 14 Jun | 740 | 691 | 2.15 | <0.05 | <2.00 | <0.10 | 0.55 | 357 | <0.50 | | 752 | <1.00 | 7.00 | 835 |
| IN17 | NP | L | 14 Jun | 740 | 691 | 2.15 | <0.05 | <2.00 | <0.10 | <0.10 | 868 | <0.50 | 0.55 | 381 | 2.57 | 4.76 | 208 |
| IN17 | NP | M | 14 Jun | 740 | 691 | 2.15 | <0.05 | 3.11 | <0.10 | <0.10 | 11 | <0.50 | 1.93 | 924 | 1.45 | 0.69 | 18 |
| IN17 | NP | K | 14 Jun | 630 | 591 | 1.25 | | | | | | | 0.95 | | | | |
| IN17 | NP | L | 14 Jun | 630 | 591 | 1.25 | <0.05 | <2.00 | 0.23 | <0.10 | 527 | <0.50 | 0.30 | 522 | 4.99 | 3.96 | 213 |
| IN17 | NP | M | 14 Jun | 630 | 591 | 1.25 | <0.05 | <2.00 | <0.10 | <0.10 | 20 | <0.50 | 1.02 | 791 | 1.96 | 0.88 | 20 |
| IN17 | NP | K | 14 Jun | 548 | 525 | 1.05 | | | | | | | 0.85 | | | | |
| IN17 | NP | L | 14 Jun | 548 | 525 | 1.05 | <0.05 | <2.00 | <0.10 | <0.10 | 654 | <0.50 | 0.23 | 263 | 2.03 | 3.89 | 123 |
| IN17 | NP | M | 14 Jun | 548 | 525 | 1.05 | <0.05 | <2.00 | <0.10 | <0.10 | 19 | <0.50 | 1.02 | 1236 | 2.63 | 0.67 | 21 |

[a] AB = Alaska blackfish, DV = Dolly Varden, AG = Arctic grayling, NP = northern pike.
[b] A blank indicates no data were collected.

**APPENDIX G: METALS CONCENTRATIONS OF KIDNEY, LIVER, AND MUSCLE AND TOTAL LENGTH, FORK LENGTH, AND WEIGHT OF CHUM SALMON (*ONCORHYNCHUS KETA*), SHEEFISH (*STENODUS LEUCICHTHYS*), AND NORTHERN PIKE (*ESOX LUCIUS*), COLLECTED FROM NOWITNA NATIONAL WILDLIFE REFUGE, ALASKA, 1991. Total and fork lengths, and weight are expressed as mm and kg, respectively.**

| | | | | | | | Metals Concentrations (mg/kg dry weight) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Site | Species[a] | Tissue | T.L. | F.L. | Wt. | Date | As | B | Be | Cd | Fe | Pb | Hg | Mg | Mn | Se | Zn |
| NO2 | CH | K | 670 | 630 | 3.1 | 28 Aug | 1.60 | <2.00 | <0.10 | 8.81 | 714 | <0.5 | 0.30 | 618 | 3.92 | 8.21 | 105 |
| NO2 | CH | L | 670 | 630 | 3.1 | 28 Aug | 1.20 | <2.00 | 0.25 | 4.96 | 639 | <0.5 | 0.30 | 521 | 7.83 | 18.10 | 270 |
| NO2 | CH | M | 670 | 630 | 3.1 | 28 Aug | 0.95 | <2.00 | <0.10 | <0.10 | 58 | <0.5 | 0.21 | 824 | <1.00 | 1.95 | 20 |
| NO2 | NP | K | 760 | 720 | 3.9 | 28 Aug | <0.50 | <2.00 | 0.37 | 0.93 | 778 | <0.5 | 1.26 | 654 | 6.39 | 7.30 | 431 |
| NO2 | NP | L | 760 | 720 | 3.9 | 28 Aug | <0.50 | <2.00 | <0.10 | 0.13 | 319 | <0.5 | 0.49 | 267 | 3.71 | 4.50 | 71 |
| NO2 | NP | M | 760 | 720 | 3.9 | 28 Aug | 0.60 | <2.00 | <0.10 | <0.10 | 61 | <0.5 | 2.00 | 1250 | 2.34 | 1.50 | 20 |
| NO2 | NP | K | 805 | 760 | 3.8 | 28 Aug | <0.50 | <2.00 | <0.10 | 0.78 | 437 | <0.5 | 1.36 | 665 | 2.22 | 6.00 | 558 |
| NO2 | NP | L | 805 | 760 | 3.8 | 28 Aug | <0.50 | <2.00 | 0.28 | <0.10 | 213 | <0.5 | 0.55 | 369 | 3.06 | 5.27 | 98 |
| NO2 | NP | M | 805 | 760 | 3.8 | 28 Aug | 1.10 | <2.00 | 0.37 | <0.10 | <5 | <0.5 | 1.85 | 1134 | 5.07 | 1.20 | 21 |
| NO2 | NP | K | 785 | 760 | 3.4 | 28 Aug | <0.50 | <2.00 | <0.10 | 0.25 | 1570 | <0.5 | 1.23 | 1164 | 6.38 | 6.00 | 192 |
| NO2 | NP | L | 785 | 760 | 3.4 | 28 Aug | <0.50 | <2.00 | <0.10 | 0.57 | 355 | <0.5 | 0.97 | 597 | 1.80 | 5.67 | 872 |
| NO2 | NP | M | 785 | 760 | 3.4 | 28 Aug | 0.90 | <2.00 | <0.10 | <0.10 | 19 | <0.5 | 1.23 | 1179 | <1.00 | 0.90 | 17 |
| NO2 | NP | L | 710 | 680 | 2.2 | 28 Aug | <0.50 | <2.00 | <0.10 | 0.10 | 248 | <0.5 | 0.30 | 213 | 3.18 | 3.44 | 98 |
| NO2 | NP | M | 710 | 680 | 2.2 | 28 Aug | 0.50 | 3.65 | <0.10 | <0.10 | 34 | <0.5 | 2.52 | 1151 | 1.16 | 1.07 | 20 |
| NO2 | NP | K | 640 | 610 | 1.7 | 28 Aug | <0.50 | <2.00 | <0.10 | 0.60 | 504 | <0.5 | 0.43 | 642 | 4.44 | 5.35 | 400 |
| NO2 | NP | L | 640 | 610 | 1.7 | 28 Aug | <0.50 | <2.00 | 0.79 | <0.10 | 406 | <0.5 | 0.12 | 701 | 2.31 | 4.59 | 100 |
| NO2 | NP | M | 640 | 610 | 1.7 | 28 Aug | 0.70 | <2.00 | 0.11 | <0.10 | 38 | <0.5 | 0.77 | 1314 | <1.00 | 1.15 | 16 |

Appenxix G. cont.

| Site | Species | Tissue | T.L. | F.L. | Wt. | Date | As | B | Be | Cd | Fe | Pb | Hg | Mg | Mn | Se | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NO4 | NP | L | 965 | 914 | 5.3 | 11 Jun | <0.50 | <2.00 | <0.10 | 0.14 | 462 | <0.5 | 1.43 | 318 | 2.00 | 5.00 | 63 |
| NO4 | NP | M | 965 | 914 | 5.3 | 11 Jun | 0.65 | <2.00 | <0.10 | <0.10 | 14 | <0.5 | 3.63 | 1089 | <1.00 | 1.18 | 16 |
| NO4 | SH | K | 780 | 720 | 3.7 | 21 Aug | <0.50 | <2.00 | 0.34 | 1.00 | 1360 | 1.3 | 5.52 | 671 | 7.38 | 8.06 | 297 |
| NO4 | SH | L | 780 | 720 | 3.7 | 21 Aug | <0.50 | <2.00 | <0.10 | 0.24 | 752 | <0.5 | 5.34 | 422 | 6.02 | 7.67 | 95 |
| NO4 | SH | M | 780 | 720 | 3.7 | 21 Aug | <0.50 | <2.00 | <0.10 | <0.10 | 34 | <0.5 | 3.76 | 1098 | <1.00 | 2.40 | 14 |
| NO4 | SH | K | 770 | 705 | 3.8 | 21 Aug | <0.50 | <2.00 | <0.10 | 0.40 | 364 | <0.5 | 1.60 | 671 | 3.40 | 6.01 | 125 |
| NO4 | SH | L | 770 | 705 | 3.8 | 21 Aug | <0.50 | <2.00 | 1.09 | 0.34 | 561 | 1.9 | 2.02 | 497 | 7.85 | 5.08 | 126 |
| NO4 | SH | M | 770 | 705 | 3.8 | 21 Aug | <0.50 | <2.00 | <0.10 | <0.10 | 39 | <0.5 | 1.15 | 918 | 1.78 | 1.40 | 13 |
| NO4 | SH | K | 950 | 885 | 6.5 | 21 Aug | <0.50 | <2.00 | <0.10 | 0.97 | 903 | <0.5 | 5.59 | 311 | <1.00 | 7.87 | 144 |
| NO4 | SH | L | 950 | 885 | 6.5 | 21 Aug | <0.50 | <2.00 | <0.10 | <0.10 | 339 | <0.5 | 4.67 | 975 | 4.66 | 5.64 | 98 |
| NO4 | SH | M | 950 | 885 | 6.5 | 21 Aug | <0.50 | <2.00 | <0.10 | <0.10 | 27 | <0.5 | 4.18 | 1202 | <1.00 | 1.97 | 12 |
| NO4 | SH | K | 940 | 870 | 7.0+ | 21 Aug | <0.50 | <2.00 | <0.10 | 0.79 | 1500 | <0.5 | 5.74 | 690 | 2.95 | 8.16 | 117 |
| NO4 | SH | L | 940 | 870 | 7.0+ | 21 Aug | <0.50 | <2.00 | <0.10 | 0.12 | 803 | <0.5 | 3.49 | 1515 | 5.41 | 4.93 | 111 |
| NO4 | SH | M | 940 | 870 | 7.0+ | 21 Aug | <0.50 | <2.00 | <0.10 | <0.10 | 35 | <0.5 | 3.01 | 959 | 1.66 | 1.16 | 14 |
| NO4 | SH | K | 880 | 830 | 5.8 | 21 Aug | <0.50 | <2.00 | <0.10 | 0.83 | 1000 | <0.5 | 3.49 | 729 | 3.93 | 7.40 | 356 |
| NO4 | SH | L | 880 | 830 | 5.8 | 21 Aug | <0.50 | <2.00 | <0.10 | <0.10 | 545 | <0.5 | 1.27 | 983 | 5.32 | 4.21 | 95 |
| NO4 | SH | M | 880 | 830 | 5.8 | 21 Aug | <0.50 | <2.00 | <0.10 | <0.10 | 33 | <0.5 | 1.87 | 978 | 1.57 | 1.20 | 14 |
| NO6 | NP | K | 390 | 354 | 0.3 | 19 Jun | [b] | | | | | | 0.23 | | | | |
| NO6 | NP | L | 390 | 354 | 0.3 | 19 Jun | | | | | | | 0.12 | | | | |
| NO6 | NP | M | 390 | 354 | 0.3 | 19 Jun | 0.60 | 2.22 | 0.11 | <0.10 | 19 | <0.5 | 0.24 | 956 | 2.68 | 0.60 | 21 |

Appendix G. cont.

| Site | Species | Tissue | T.L. | F.L. | Wt. | Date | As | B | Be | Cd | Fe | Pb | Hg | Mg | Mn | Se | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NO6 | NP | K | 802 | 760 | 3.1 | 19 Jun | <0.50 | <2.00 | <0.10 | 1.64 | 250 | 2.0 | | 707 | 4.35 | 6.10 | 485 |
| NO6 | NP | L | 802 | 760 | 3.1 | 19 Jun | <0.50 | <2.00 | <0.10 | 0.91 | 252 | <0.5 | 3.29 | 821 | <1.00 | 7.42 | 290 |
| NO6 | NP | M | 802 | 760 | 3.1 | 19 Jun | 1.10 | 2.10 | <0.10 | <0.10 | <5 | <0.5 | 4.66 | 1151 | 1.50 | 0.51 | 14 |
| NO6 | NP | K | 500 | 472 | 0.6 | 19 Jun | | | | | | | 0.64 | | | | |
| NO6 | NP | L | 500 | 472 | 0.6 | 20 Jun | | | | | | | 0.33 | | | | |
| NO6 | NP | M | 500 | 472 | 0.6 | 19 Jun | 0.85 | <2.00 | <0.10 | <0.10 | <5 | <0.5 | 0.72 | 1086 | 2.69 | 0.60 | 24 |

[a] CH = chum salmon, SH = sheefish, NP = northern pike.
[b] A blank indicated that no data were collected.

## APPENDIX H: LITERATURE CITED FOR APPENDICES

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