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TECHNICAL REPORT

METAL AND METALLOID CONTAMINANTS IN WATER, SEDIMENTS, FISH, AND MAMMALS OF KANUTI NATIONAL WILDLIFE REFUGE, ALASKA, 1985 - 1990

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Fish and Wildlife Service
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EXECUTIVE SUMMARY

This study was conducted by U.S. Fish and Wildlife Service biologists from 1985 through 1990. The study goals were to monitor water quality as well as concentrations of metals and metalloids in water, stream sediments, fish, and mammals; evaluate existing effects of heavy metal contamination and water quality degradation on refuge resources due to placer mining; and make recommendations for collection of additional baseline data to protect water quality, conserve fish and wildlife populations and their habitats, and to protect subsistence use, consistent with refuge goals. Water samples were collected from 32 sites; 16 sites on Kanuti National Wildlife Refuge and 16 sites upstream from it.

Mineral deposits of many types have been located in the vicinity of the refuge. These include antimony, copper, lead, gold, nickel, silver, tin, and zinc. Extraction of these resources could affect fish and wildlife resources of the refuge, downstream of these deposits. Placer mining for gold has occurred in all major drainages that enter the refuge.

The South Fork Koyukuk River is a clear, soft water, calcium and magnesium bicarbonate-dominated stream with near neutral pH. Samples from South Fork tributary streams indicate that Bonanza, Fish, and Prospect creeks, and the Jim River, had lower hardness and alkalinity than the main stem. Samples from the Koyukuk River were slightly alkaline in pH, moderate in hardness and, unlike samples from the South Fork Koyukuk River, had almost twice the concentration of cations comprising hardness as anions comprising alkalinity. Samples from Koyukuk River tributary streams, the John and Wild rivers, had similar water quality characteristics as the main stem. Values of pH, conductivity, hardness, and alkalinity were generally higher in samples from the Middle Fork Koyukuk River than in those from the South Fork Koyukuk or Koyukuk rivers. Like Koyukuk River samples, samples from the Middle Fork Koyukuk River had a high hardness to alkalinity ratio. Similar to the South Fork Koyukuk River, Kanuti and Kanuti-Kilolitna river samples had soft, low alkalinity, clear water. All measurable settleable solids and, with few exceptions, high turbidity and suspended solids measurements were taken during the June 24-25, 1985 and May 25-26, 1987 sample periods, that were periods of high rainfall.

Surface waters examined during this study were relatively uncontaminated by metals. Arsenic, cadmium, chromium, and thallium were either not detected or detected in very low concentrations. Iron concentrations exceeded the chronic Environmental Protection Agency Criteria for the Protection of Aquatic Life in many instances and may be affecting fish spawning success in the greater Koyukuk River drainage. In general, Koyukuk River samples had the highest total arsenic, copper, iron, lead, manganese, nickel, and zinc concentrations in water. The Koyukuk River likely has higher concentrations of these metals, because particulates are more highly mobilized in this river than in the other rivers we sampled. Concentrations of total copper, iron, manganese, nickel, and zinc were highly correlated with turbidity for 1985, and concentrations of total aluminum, iron, and manganese were highly correlated with turbidity and suspended solids for 1988.

We found concentrations of arsenic, cadmium, copper, lead, and nickel to be generally within the upper portion of ranges listed as uncontaminated sediments. Mercury was rarely detected in sediments and when detected, was near the limit of detection. Koyukuk River samples generally had higher concentrations of metals in sediment than samples from the South Fork Koyukuk River drainage. Wild River sediments had the highest values of arsenic, barium, cadmium, copper, lead, nickel, thallium, vanadium, and zinc, and the second highest value of iron for sites sampled during 1988.

Longnose sucker (*Catostomus catostomus*), least cisco (*Coregonus sardinella*), and slimy sculpin (*Cottus cognatus*) accumulated metals to differing degrees. Least cisco accumulated aluminum, copper, iron, lead, manganese, and nickel; longnose sucker accumulated cadmium and copper; and slimy sculpin accumulated aluminum, barium, cadmium, copper, iron, lead, manganese, strontium, and zinc more than other species. Northern pike (*Esox lucius*) had the highest mercury concentrations.

Cadmium, copper, magnesium, mercury, nickel, selenium, and zinc accumulated differentially in tissue, with cadmium concentrations in kidney> liver> muscle and copper concentrations in liver> kidney> muscle. For longnose sucker and northern pike magnesium concentrations in kidney were significantly greater than in liver and muscle. Nickel concentrations in longnose sucker kidney, during 1987, were significantly greater than in muscle. The pattern of mercury accumulation was not consistent. During 1985 mercury concentrations were greatest in kidney; however, during 1986, 1987, and 1988 they were greatest in muscle. In 1988, zinc concentrations in kidney were significantly greater than in liver (longnose sucker) and muscle (longnose sucker and northern pike).

Whole body concentrations of arsenic and cadmium in northern pike and Arctic grayling (*Thymallus arcticus*) did not exceed the 1984 National Contaminant Biomonitoring Program (NCBP) 85th percentile concentrations. Composite slimy sculpin samples exceeded the NCBP 1984 85th percentile concentrations for cadmium (7 of 7 samples), lead (10 of 10 samples), and zinc (8 of 9 samples). Mercury was detected in each fish sampled regardless of location. Mercury concentrations in whole body, muscle, kidney, and liver samples from this study were within the range reported for uncontaminated conditions. Nickel was detected sporadically in fish tissue between <0.9-9.13 mg/kg, with high concentrations observed in Arctic grayling, least cisco, and northern pike.

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INTRODUCTION

Established by the Alaska National Interest Lands Conservation Act of 1980 (ANILCA), Kanuti National Wildlife Refuge in northcentral Alaska includes approximately 662,000 ha (1.64 million acres) of land (U.S. Fish and Wildlife Service [USFWS] 1987). The refuge is located in a basin formed by the Kanuti and Koyukuk rivers, with the Brooks Range to the north and the Ray Mountains to the south, and is bisected by the Arctic Circle (Figure 1). No wilderness areas have been established within the refuge. As part of the 1971 Alaska Native Claims Settlement Act, approximately 140,000 ha (345,000 acres) within the refuge boundary have been selected by or conveyed to Alaska Native village corporations and Native groups. Four communities lie just outside the refuge boundary: Bettles and Evansville, to the north, and Alatna and Allakaket, to the west.

The refuge landscape consists primarily of rolling hills, wetlands, ponds, and streams. The most biologically productive portion of the refuge is Kanuti Flats which constitutes the central portion of the refuge (USFWS 1987). This area supports the majority of the wildlife, on the refuge.

The purposes of Kanuti Refuge are:

> (1) to conserve fish and wildlife populations and habitats in their natural diversity including, but not limited to, white-fronted geese (*Anser albifrons*) and other waterfowl and migratory birds, moose (*Alces alces*), caribou (*Rangifer tarandus*) (including participation in coordinated ecological studies and management of the Western Arctic Caribou Herd), and furbearers;
>
> (2) to fulfill the international treaty obligations of the United States with respect to fish and wildlife, and their habitats;
>
> (3) to provide, in a manner consistent with the purposes set forth above, the opportunity for continued subsistence uses by local residents; and
>
> (4) to ensure, to the maximum extent practicable and in a manner consistent with the purposes set forth in (1) above, water quality and necessary water quantity within the refuge (USFWS 1987).

Identified special values of the Kanuti Refuge include: Hulgothen Bluffs, Kanuti Canyon, Sithylemankat Lake, the subsistence way of life for residents of the area, and cultural resources. Refuge lakes and rivers support both anadromous and freshwater fisheries. Fish species used for sport and subsistence fishing within the refuge include sheefish (*Stenodus leucichthys*), northern pike (*Esox lucius*), whitefishes (*Coregonus* spp.), Arctic grayling (*Thymallus arcticus*), Dolly Varden (*Salvelinus malma*), chinook salmon (*Oncorhynchus tshawytscha*), chum salmon (*Oncorhynchus keta*), and silver salmon (*Oncorhynchus kisutch*).

Approximately 150 species of birds have been documented on the Kanuti refuge including Canada geese (*Branta canadensis*) and white-fronted geese, bald eagles (*Haliaeetus leucocephalus*), and peregrine falcons (*Falco peregrinus*). Refuge wetlands support high densities of breeding waterfowl and other waterbirds.

Surficial deposits within the refuge have been heavily influenced by glaciation. The types of surficial deposits include glacial, alluvial, lacustrine, colluvial, and eolian (USFWS 1987). Glaciers have not only redistributed and reformed surface sediments, they have produced large,

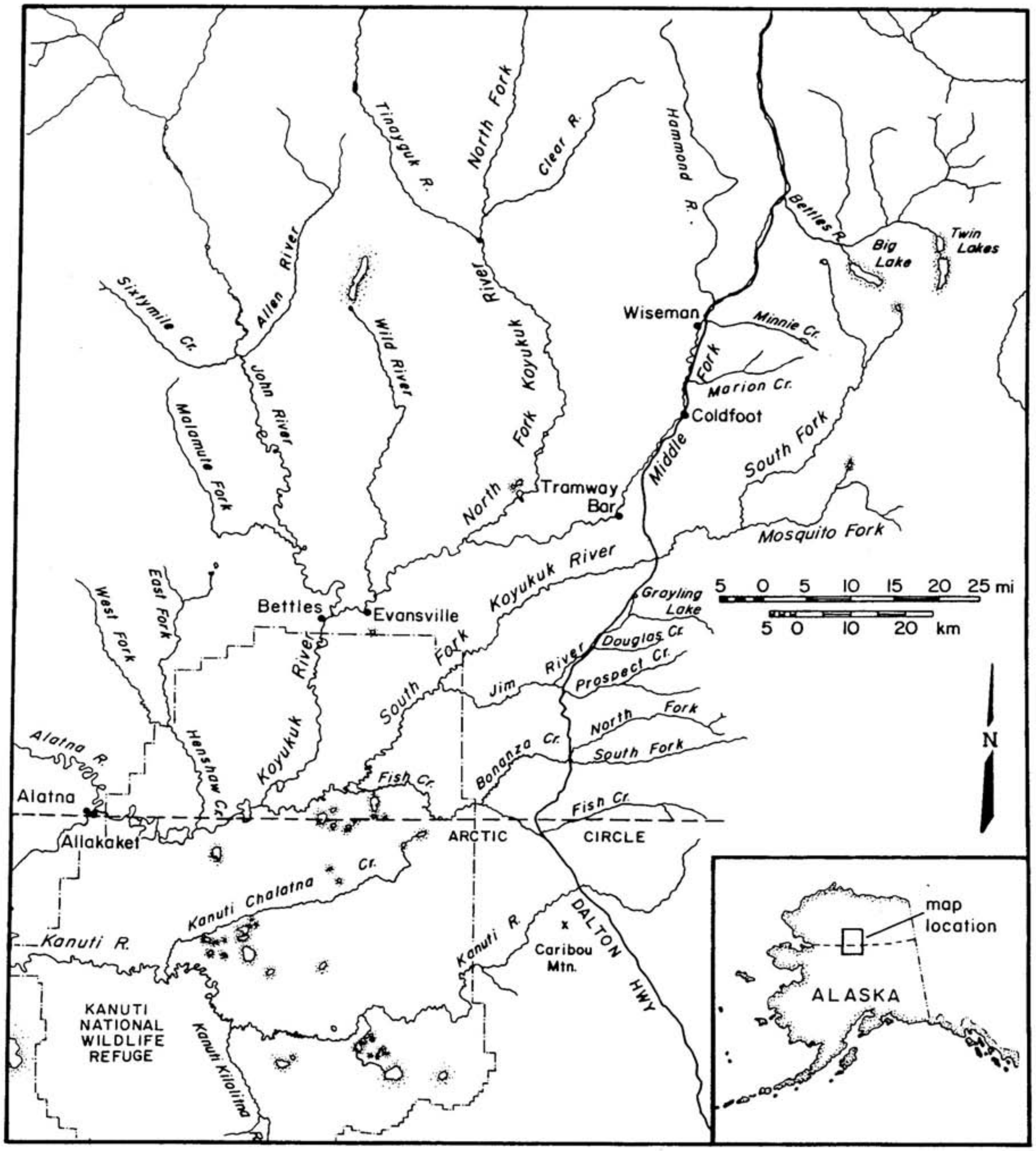

Figure 1. Location of Kanuti National Wildlife Refuge, Alaska.

e.g., 520 and 780 km^2 (200 and 300 miles^2), lakes by damming rivers, reversed drainages, and made silt outwash available for wind transport and redeposition. After glaciation, refuge lowlands were probably left with wide areas of soft silt and mud. The most recent sediments on the refuge are the channel, floodplain, and lower terrace alluvium of the existing larger watercourses (USFWS 1987).

Geologically, the Kanuti Refuge is in the northeastern corner of the Yukon/Koyukuk Volcanic Province. Mineral deposits of many types have been located on and upstream of the refuge (Figure 2). Ultramafic rocks are commonly enriched in chromium, nickel, cobalt and platinum. Six pods of ultramafic rocks containing chromite are located within and adjacent to the refuge (Patton and Miller 1970, 1973). Gold has been found in many areas upstream of the refuge, chiefly to the north and northeast. Cobb (1972a, b, c) notes gold discoveries at 12 locations in the Wild River drainage, 34 locations in the Middle Fork Koyukuk River drainage, and 16 locations in the South Fork Koyukuk drainage. Cobb (1972b) notes four occurrences of copper, two of lead, and one of antimony in the Wild River drainage. The John River drainage has five occurrences of copper, three of lead, and one of antimony (Cobb 1972b). The Middle Fork Koyukuk River has three occurrences of copper, two each of lead and silver, and five of antimony (Cobb 1972b, c). The South Fork Koyukuk River has 11 occurrences of copper, 3 of nickel, 2 each of silver, mercury and lead, and 1 of tin and zinc (Cobb 1972a, c). The headwater area of the Kanuti-Kilolitna River is reported to have good potential for large, low-grade tin-tungsten-tantalum-niobium placer deposits (USFWS 1987). The Kanuti River drainage has one occurrence each of silver, lead and zinc (Cobb 1972a).

Section 304(g)(2E) of ANILCA mandates identification and description of problems which may adversely affect refuge fishery resources and wildlife populations. Potential problems affecting fish and wildlife and their habitats identified in the Comprehensive Conservation Plan (USFWS 1987) include increased public use, development of the extensive inholdings and adjacent private land, and mining on adjacent lands. Commercial developments on adjacent lands could adversely affect the refuge's scenic, air, and water resources, as well as restrict the opportunities for subsistence. The Alyeska oil pipeline and Dalton Highway, located a few miles east of the refuge, cross four rivers draining into the refuge, increasing the likelihood that oil spills or other contaminants could enter the refuge. Placer gold or other types of mining on inholdings and near refuge boundaries also could potentially affect water quality, fish and wildlife populations, and their habitats within the refuge. No known valid mining claims occur within the refuge (USFWS 1987) (Figure 3).

Placer mining for gold has occurred in all major drainages that enter the refuge. Placer gold was first found, in this area, between 1885 and 1890 on bars of the Koyukuk River and some of its tributaries. The first major discoveries were on Myrtle Creek and the Hammond River in 1899 and 1900, respectively (Cobb undated). By 1910, gold was being produced from many sites in the Koyukuk River drainage (Bliss et al. 1988) and placer gold has been mined in every year since that time. Until 1961, more than 85% of all placer gold mined in the vicinity of the refuge came from a small area north of and within 10 miles of Wiseman, particularly Nolan and Vermont creeks, tributaries of the Middle Fork Koyukuk and Hammond rivers, respectively. Other areas with high mining activity were at Wild Lake on tributaries of the Wild River, tributaries of the Middle Fork Koyukuk River near Coldfoot and Big Lake, and on bars of the Middle Fork Koyukuk and South Fork Koyukuk rivers (Cobb undated).

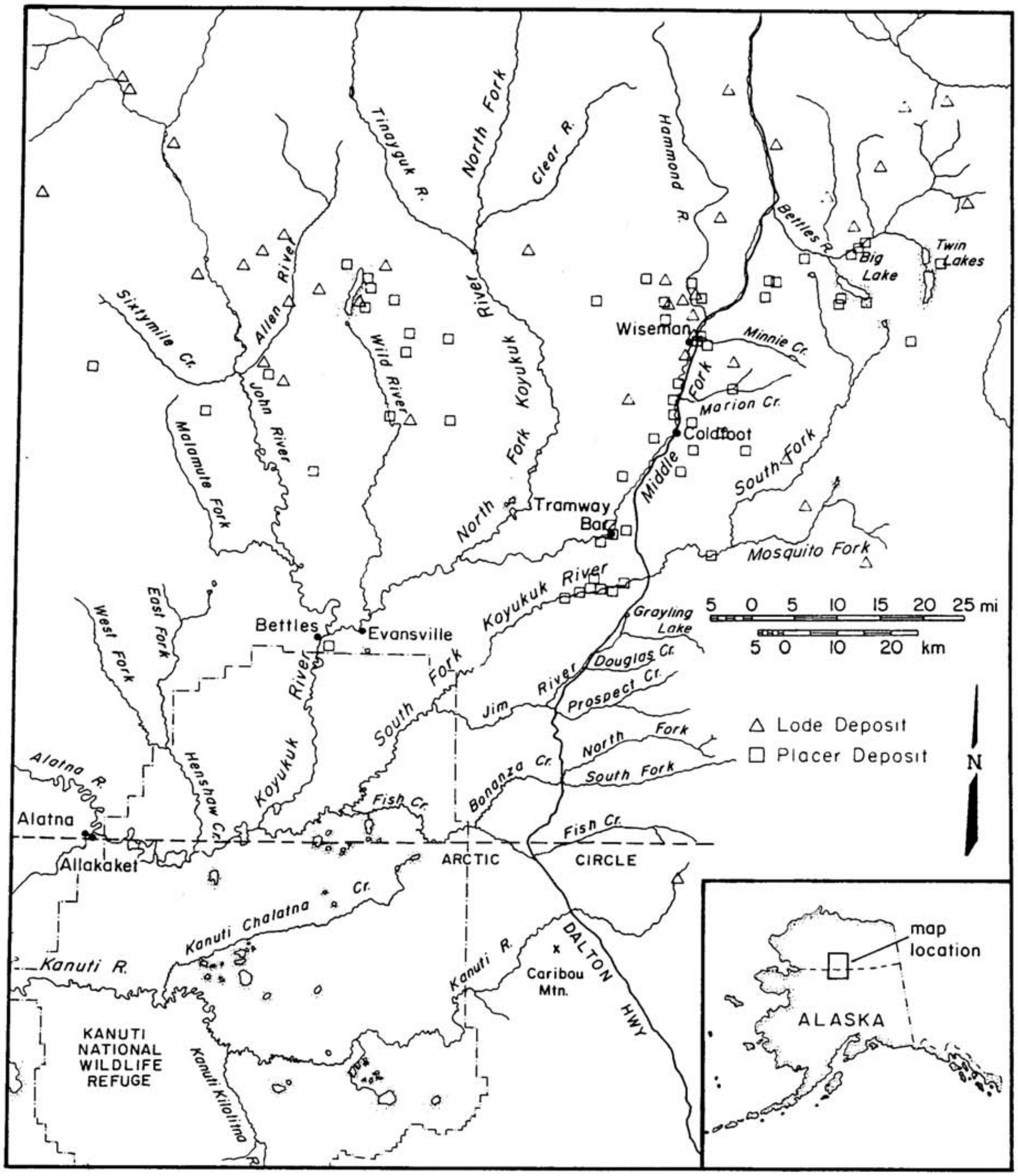

Figure 2. Documented mineral occurrences near Kanuti National Wildlife Refuge, Alaska.

Frequently, large amounts of overburden are removed to extract gold from ancient alluvia. Mined sediment-rich effluent, transported in suspension and as bedload, may cause elevated turbidities in the water column and blanket the stream bottom, making it unsuitable for benthic aquatic life (Bjerklie and LaPerriere 1985; LaPerriere et al. 1985; Wagener and LaPerriere 1985; Weber and Post 1985; Van Nieuwenhuyse and LaPerriere 1986; Lloyd 1987; Lloyd et al. 1987; Weber Scannell 1992). In addition, mining activities may mobilize trace metals such as arsenic, cadmium, copper, lead, mercury, and zinc, thus making them more available for biologic uptake (LaPerriere et al. 1985). These metals can be toxic to aquatic organisms in the receiving streams. Since 1985, Environmental Protection Agency (EPA) requirements for 100 percent recycling of process water during medium- and large-scale placer mining have significantly lessened, but not eliminated, these problems in Alaska (Alaska Department of Environmental Conservation 1991).

Our objectives for this study were to:

1. Monitor water quality and concentrations of heavy metals in water, stream sediments, mammal hair, and fish at sites within the refuge, and upstream of the refuge.

2. Evaluate existing effects of heavy metal contamination and water quality degradation on refuge water, sediments, and fish due to placer mining.

3 .Recommend studies needed to complete a baseline data set for the protection of water quality, to conserve fish and wildlife populations and their aquatic-based habitats, and to protect subsistence use, consistent with refuge goals.

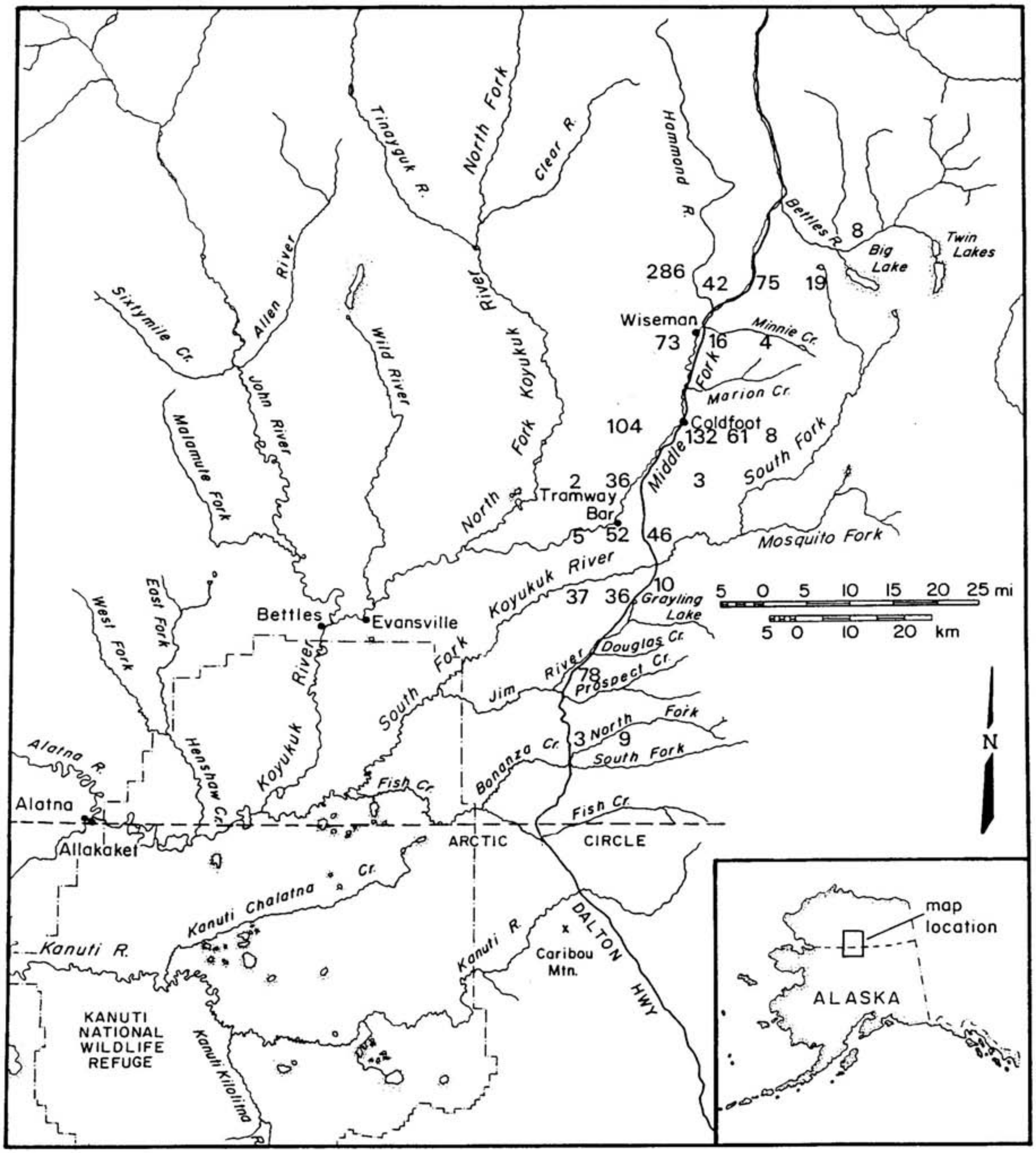

Figure 3. Location of active mining claims in drainages flowing into Kanuti National Wildlife Refuge. Numbers indicate number of active mining claims in each township.

METHODS AND MATERIALS

Sample Sites

Samples were collected from 32 sites, 16 within the Kanuti Refuge and 16 off the refuge (Figure 4). In addition, mammal hair samples were collected on a trapline in the John River drainage. Sample site descriptions are as follows.

Site 1, Koyukuk River at Bettles Field (the Yacht Club), T. 24 N, R. 18 W, Sec. 8, NW 1/4, Fairbanks Meridian (FM), 66°00'20" N, 151°31'20" W.

Site 2, Koyukuk River at the refuge boundary with Doyon lands, T. 22 N, R. 19 W, Sec. 5, NE 1/4, FM, 66°46'00" N, 151°42'15" W.

Site 3, South Fork Koyukuk River just above the confluence with the Koyukuk River (Union City Slough), T. 20 N, R. 20 W, Sec. 6, SW 1/4, FM, 66°34'50" N, 151°55'20" W.

Site 4, Koyukuk River at the confluence with the South Fork Koyukuk River, T. 20 N, R. 21 W, Sec. 1, SW 1/4, FM, 66°35'00" N, 151°57'40" W.

Site 5, South Fork Koyukuk River just above the mouth of Fish Creek, T. 21 N, R. 19 W, Sec. 36, NW 1/4, FM, 66°31'37" N, 151°35'20" W.

Site 6, Fish Creek just above the confluence with the South Fork Koyukuk River, T. 21 N, R. 19 W, Sec. 36, NW 1/4, FM, 66°31'37" N, 151°35'05" W.

Site 7, South Fork Koyukuk River at old Soo City town site, T. 21 N, R. 18 E, Sec. 3, SE 1/4, FM, 66°40'08" N, 151°25'28" W.

Site 8, Fish Creek just below the mouth of an unnamed creek flowing from the largest (unnamed) lake in the section, T. 21 N, R. 17 W, Sec. 30, NE 1/4, FM, 66°37'30" N, 151°20'30" N, 151°20'00" W.

Site 9, South Fork Koyukuk River just downstream of the Dalton Highway, T. 25 N, R. 13 W, Sec. 34, FM, 67°01'12' N, 150°19'00" W.

Site 10, South Fork Koyukuk River just downstream from the Gold Bench mine site, T. 25 N, R. 15 W, Sec. 19, S. 1/2, FM, 66°58'33" N, 150°42'50" W.

Site 11, South Fork Koyukuk just upstream from the Gold Bench mine site, T. 25 N, R. 14 W, Sec. 21, NE 1/4, FM, 66°59'00" N, 150°37'28" W.

Site 12, South Fork Koyukuk just above the confluence with the Jim River, T. 23 N, R. 17 W, Sec. 22, SE 1/4, FM, 66°47'10" N, 151°12'20" W.

Site 13, Jim River just above the confluence with the South Fork Koyukuk River, T. 23 N, R. 17 W, Sec. 26, SW 1/4, FM, 66°47'20" N, 151°11'50" W.

Site 14, Kanuti River just below the mouth of an unnamed creek flowing from Tokusataquaten Lake, T. 16 N, R. 17 W, Sec. 14, NW 1/4, FM, 66°13'04" N, 151°04'57" W.

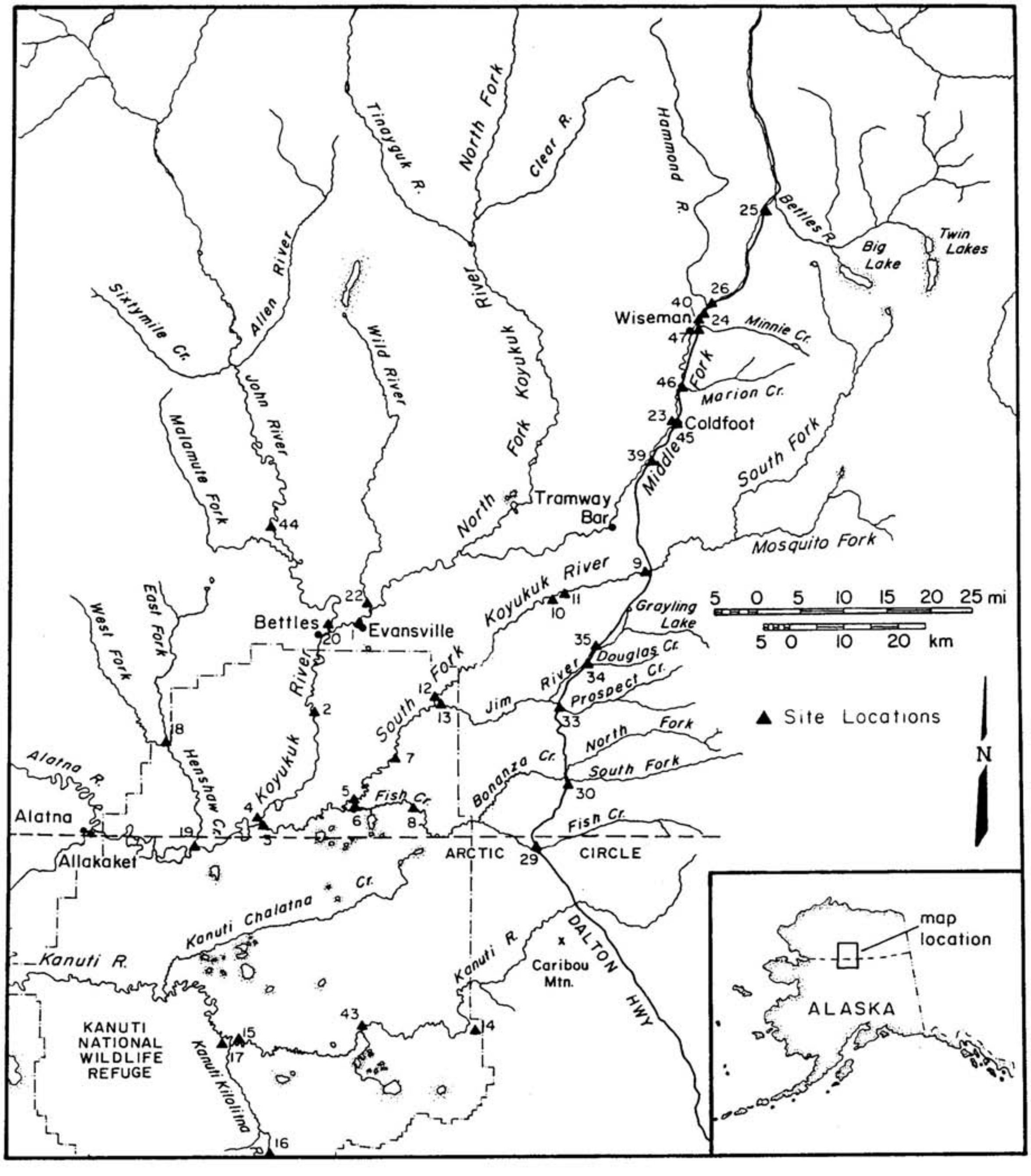

Figure 4. Map of Kanuti National Wildlife Refuge, Alaska, showing sample sites.

Site 15, Kanuti River just above the confluence with the Kanuti Kilolitna River, T. 16 N, R. 21 W, Sec. 20, NE 1/4, FM, 66°12'20" N, 152°02'08" W.

Site 16, Kanuti Kilolitna River at the refuge boundary, T. 14 N, R. 20 W, Sec. 31, Central W. 1/2, FM, 66°00'01" N, 151°51'45" W.

Site 17, Kanuti Kilolitna River just above the confluence with the Kanuti River, T. 16 N, R. 21 W, Sec. 20, NE 1/4, FM, 66°12'45" N, 152°02'25" W.

Site 18, Henshaw Creek at the confluence of the East and West Forks, T. 22 N, R. 22 W, Sec. 21, SE 1/4, FM, 66°42'48" N, 152°19'30" W.

Site 19, Henshaw Creek just above the confluence with the Koyukuk River, T. 20 N, R. 22 W, Sec. 23, NW 1/4, FM, 66°33'00" N, 152°13'00" W.

Site 20, John River just upstream of its confluence with the Koyukuk River, T. 24 N, R. 19 W, Sec. 10, FM, 66°55'50" N, 151°40'00" W.

Site 22, Wild River just upstream of its confluence with the Koyukuk River, T. 25 N, R. 18 W, Sec. 13, FM, 67°00'00" N, 151°24'40" W.

Site 23, Middle Fork Koyukuk River at Coldfoot, T. 28 N, R. 12 W, Sec. 16, FM, 67°30'00" N, 150°12'00" W.

Site 24, Middle Fork Koyukuk River at the Dalton Highway, 0.40 kilometers below the mouth of the Hammond River, T. 30 N, R. 11 W, Sec. 5, FM, 67°27'35" N, 150°02'36" W.

Site 25, Middle Fork Koyukuk River just below the mouth of the Bettles River, T. 32 N, 10 W, Sec. 9, FM, 67°37'00" N, 149°46'36" W.

Site 26, Middle Fork Koyukuk River just above the mouth of the Hammond River, T. 30 N, R. 11 W, Sec. 4, FM, 67°27'35" N, 150°01'50" W.

Site 29, Fish Creek at the Dalton Highway, T. 20 N, R. 15 W, Sec. 20, FM, 66°32'18" N, 150°46'47" W.

Site 30, South Fork Bonanza Creek at the Dalton Highway, T. 21 N, R. 14 W, Sec. 7, FM, 66°39'43" N, 150°39'23" W.

Site 33, Prospect Creek at the Dalton Highway, T. 23 N, R. 14 W, Sec. 31, FM, 66°46'56" N, 150°41'05" W.

Site 34, Douglas Creek at the Dalton Highway, T. 24 N, R. 14 W, Sec. 34, FM, 66°51'23" N, 150°33'20" W.

Site 35, Jim River at the Dalton Highway, T. 24 N, R. 14 W, Sec. 23, FM, 66°53'05" N, 150°31'09" W.

Site 39, Rosie Creek at the Dalton Highway, T. 27 N, R. 13 W, Sec. 6, FM, 67°11'45" N, 150°16'36" W.

Site 40, Middle Fork Koyukuk River at the Dalton Highway, T. 30 N, R. 11 W, Sec. 7, FM, 67°26'18" N, 150°04'36" W.

Site 43, Kanuti River at T. 16 N, R. 19 W, Sec. 11, FM, 66°14'04" N, 151°30'00" W.

Site 44, John River at T. 26 N, R. 20 W, FM, 67°08'51"N, 151°05'42"W.

Site 45, Slate Creek at the Dalton Highway, T. 28 N, R. 13 W, Sec. 15, FM, 67°16'12" N, 150°0'30" W.

Site 46, Marion Creek at the Dalton Highway, T. 29 N, R. 12 W, Sec. 23, FM, 67°19'42" N, 105°9'45" W.

Site 47, Minnie Creek at the Dalton Highway, T. 30 N, R. 11 W, Sec. 18, FM, 67°25'24" N, 150°4'30" W.

Water, sediment, and tissue samples were collected annually from 1985 to 1990. Samples of water were collected and analyzed for various water quality variables, and dissolved, total recoverable (weak-acid digestion) and total (complete acid digestion) metals and metalloids. In addition, sediments, fish tissues, and mammal hair samples were collected for metal and metalloid analysis. Samples collected, except mammal hair, and sites sampled are listed in Table 1. Three marten (*Martes americana*) hair samples were collected from a trapline nearest Site 10 during 1989 and 14 wolf (*Canis lupus*) hair samples were collected from a trapline nearest Site 44 during 1990.

Collection Methods and Field Analyses

Water

Water quality samples. Water quality data were collected during one or more sample periods from May through August, 1985 - 1990. Triplicate 1-L grab samples were collected in 1987 and 1988. Single 1-L grab samples were collected for all other years. All water samples were collected just below the water surface. Samples were filled to the top of the bottle to minimize gaseous exchange. Each sample bottle was labeled immediately prior to collection and placed in a cooler with ice or snow for transport to a field laboratory for analysis.

Samples were analyzed for the following water quality variables: pH, total alkalinity, total hardness, conductivity, turbidity, suspended solids, and settleable solids. During 1987, samples were also analyzed for dissolved oxygen. During 1990, samples were not analyzed for total alkalinity and suspended solids. Hardness and alkalinity determinations were made using a Hach digital titrator and either Hach (1985) methods or Standard Methods (APHA et. al. 1981) (1985 only) with colorimetric endpoints. 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 either a Hach Digital 19000 (1985) pH meter or an Orion Model SA250 pH meter (1987-1990). Both meters were 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.

Table 1. Site locations of samples collected from Kanuti National Wildlife Refuge, Alaska, 1985 - 1990.

Year	Water Quality	Total Metals	Total Recoverable Metals	Dissolved Metals	Sediment Metals	Fish Tissue Metals
1985	1-8, 10-13	1-5, 7	1-6, 8	1-5, 7	1-5, 7-9	1, 3, 5, 7, 8
1986						14-19
1987	1-7, 10-13	1-7, 10-13	1-7, 10-13	1-7, 10-13	1-7, 10-13	1-3, 5-7, 10-13
1988	2, 20, 22-26	2, 20, 22-26	2, 20, 22-26	2, 20, 22-26	2, 20, 22-26	1, 20, 22, 23
1989	1, 2, 5, 6, 15, 17, 19, 20, 22, 43					1-6, 15, 17, 19, 20, 22, 43
1990	9, 29, 30, 33, 35, 39, 40, 45-47					9, 29, 30, 33, 35, 39, 40, 45-47

Three 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). Samples for total suspended solids analysis were sent to a commercial laboratory for analysis. Total settleable solids were measured using the Imhoff Cone Method for 1-L samples (APHA et al. 1981, 1989). If settleable solids occurred, but did not exceed 0.1 mL/L, "trace" was recorded.

Trace elements samples. Water samples for metals analysis were surface grab samples collected in triplicate in the same manner as the water quality samples. Unfiltered, acidified samples were collected for total metals and total recoverable metals analysis, and filtered, acidified samples were collected for dissolved metal analysis. Dissolved metals samples were filtered in the field using 0.8 µm prefilters and either 0.45 µm Millipore filters and pump (1985), or 0.45 µm cellulose acetate syringe filters with Luerlock fittings (1987, 1988) in the field. The volume of filtered sample was approximately 250-mL. Samples for total metals, total recoverable metals, and dissolved metals analysis were acidified to a pH <2 with either 1-1.5 mL (1985) or 2-mL (1987, 1988) HNO_3 (Ultrix). All trace metal water samples were collected in previously unused 500-mL acid-precleaned high-density polyethylene bottles from either the Environmental Protection Agency (EPA) (1985) or I-Chem (1987, 1988).

Sediments

Either one (1985) or three (1987 and 1988) composite sediment samples were collected from shore at each site where sediment samples were collected. Samples were collected using either Nalgene bottles (1985), also used for sample storage, or a stainless steel strainer (1987, 1988). Samples collected using the stainless steel strainer were transferred to new acid-cleaned 500-mL I-Chem polyethylene bottles with teflon-lined lids. Fine silt was sought for sampling in all cases. Each sample bottle was labelled immediately prior to collection and placed in a cooler with ice or snow for transport to a freezer.

Fish Tissues

Fish were collected by angling (1986, 1987, 1989), experimental monofilament gillnet (1985, 1986, 1987, 1989), and electroshocker (1989, 1990). Target fish species included adult slimy sculpin (*Cottus cognatus*), Arctic grayling, and northern pike; however, longnose sucker (*Catastomus catastomus*), least cisco (*Coregonus sardinella*), humpback whitefish (*Coregonus pidschian*), whitefish (*Coregonus* sp.), and lake chub (*Couesius plumbeus*) were also caught and analyzed. Fish samples were weighed to the nearest gram, and total and fork lengths were measured to the nearest millimeter (1987, 1988, 1989). Liver, kidney, and muscle samples were dissected, using stainless steel instruments, from each fresh caught fish longer than approximately 400 mm. Samples were transferred to previously unused, acid-precleaned Nalgene (1985) or 60-mL I-Chem (1988, 1989) bottles. Fish shorter than 400 mm were stored in double ziplock bags (1988, 1989). In 1987, whole fish were sent to the laboratory for dissection and analysis, or analysis as whole fish; fish longer than approximately 400 mm were double-wrapped in freezer paper. Small fish were pooled to make a sample. Each sample was labelled immediately prior to collection and placed in a cooler with ice for transport to a freezer.

Sample Handling and Labelling

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

Prior to data interpretation, field sample identifiers were converted into a 10-digit identification number using designated alphanumeric fields, as described in Appendix B. Trace element data for these samples were then entered into a contaminants data management system, using DBase IV software, 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 database data.

Laboratory Analyses

Prior to analysis, each sediment sample was freeze-dried, except in 1987 when sediments were air-dried, sieved to remove large particles, and homogenized by grinding in a mortar and pestle. Fish tissues were also freeze-dried, and homogenized using either a food processor or a Spex Industries Inc. Model 8000 mixer/mill (1989), followed by digestion and analysis.

Samples for inductively coupled argon plasma spectroscopy (ICP) analysis were digested as follows: either concentrated nitric acid or a mixture of concentrated nitric and concentrated perchloric acids for tissue; a mixture of concentrated nitric and hydrochloric acids for total water; a mixture of dilute nitric and hydrochloric acids for total recoverable water; and a mixture of dilute nitric, perchloric, and hydrochloric (1985) acids for sediment. Samples for mercury analysis were digested with nitric acid according to Monk (1961) and analyzed by cold vapor atomic absorption spectrophotometry. Arsenic and selenium for all years, lead for 1988, and antimony for 1990 were analyzed by flameless atomic absorption spectrophotometry using a graphite furnace. Samples for graphite furnace analysis were digested using nitric acid. Samples for other metals were analyzed using ICP, with preconcentration for water and tissue samples. However, tissues collected in 1988 were analyzed using ICP without preconcentration. ICP samples were analyzed according to Standard Methods (APHA et al. 1981, 1989). Tissue data are expressed as mg/kg dry weight.

Quality Assurance - Quality Control

Field Collections

Water samples were collected in new, precleaned containers from either I-Chem or EPA using protocols designed to reduce the potential of sample contamination. These included precautions to avoid direct contact between the sample container or sample and the collector or other sources of contamination. Where appropriate, samples were preserved in the field. All samples were stored in coolers with ice in the field and frozen or refrigerated on their return from the field, as appropriate. Samples were shipped to contract laboratories in coolers containing ice or blue ice.

Water quality sample containers were triple-rinsed in the river water to be sampled prior to sampling. Water quality measurements were performed on the same day as collection with the exception of the suspended solids measurements, which were performed by a commercial analytical laboratory at a later date. 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. Suspended solid measurements were also subject to performance checks using EPA check samples. Sample locations and sample numbers were assigned prior to field sampling. Water samples were collected by direct surface grabs into the current. During 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.

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. Composite samples consisting of three to four grabs each constituted a single replicate sample. Each sample was homogenized with a glass rod prior to transfer to the storage container. During sediment collection, care was taken to avoid any contact between the sample and hands or footwear. Samples were frozen following collection and shipped to the laboratory in coolers with dry ice by overnight air courier.

Fish were rinsed with river water from the site of collection or distilled water to minimize external contamination. Morphometric measurements were made on site, except in 1987 when morphometric measurements were made in the field laboratory. Dissections of kidney, liver, and dorsal muscle were performed by the collector in the field, except in 1987 when fish were shipped to the analytical laboratory for dissection under clean conditions. Dissections were performed with stainless steel and teflon dissection equipment on a clean metal-free surface, with new carbon steel blades used for each tissue sample. Tissues were immediately placed in storage containers. Small fish (usually < 300 mm) were placed in either double Ziplock bags or new precleaned I-Chem bottles. Smaller fish were analyzed as whole fish, including the gut and gut contents. Samples were shipped to the laboratory in coolers with dry ice by overnight air courier.

Laboratory AnalysesLaboratory 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. Tables 2 - 4 identify acceptable analytical data sets for water, 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 <20%, spike recovery 80 - 120%, SRM within 3 standard deviations of the certified mean, and blank <15% of the mean duplicate value or <LOD. Spike and SRM analyses were not available for hair analyses, therefore, the QC for these analyses is based on blank and duplicate sample analyses.

The USFWS Patuxent Analytical Control Facility (PACF) determined that the analytical laboratories used for the 1988 water samples and the 1990 fish samples did not produce sufficient QA-QC data for them to estimate confidence intervals. Estimated 95% confidence intervals for 1987, 1988 sediment and tissue, 1989 tissue, and 1990 hair sample analyses are listed in Table 5.

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.

Concentrations of some analytes were higher for total recoverable and dissolved metals than for total metals. This unacceptable situation may be caused either by the addition of metals to the dissolved samples during filtration or preservation, or by sampling or analytical error. In these cases, the results were omitted from this report. All of the dissolved lead data for 1987 were greater than the total lead data of that year. Except for the lead data, all total recoverable metals data from Site 12 for 1987 were greater than the total metals data. For 1988, total recoverable arsenic, nickel, selenium, and thallium were not detected except in concentrations greater than the corresponding total metals analysis.

Lead and nickel data for 1990 fish tissue had an RPD of 21% and a spike recovery of 121%, respectively, and, therefore, did not meet the QA-QC criterion of 20% and 120%, respectively, for these variables. However, these data are used with qualification. Water samples for mercury were held longer than the maximum recommended holding time (APHA et al. 1989) and, the resultant analytical data were discarded.

Statistical Analyses

Values <LOD were replaced by one-half the LOD for statistical analyses. Data sets containing greater than one-half of the values <LOD were not subjected to statistical analysis. Statistical analyses were performed on SPSS/PC+ statistical software.

Data set means were compared using the one-way analysis of variance (for three or more sample sets) and the Student t test (for two sample sets). Some data sets contained variables that did not meet the requirements for use of parametric statistics; i.e., distributions were not normal or variances were not homogenous. In these instances, the Kruskal-Wallis test for three or more samples was used. The Scheffe' multiple range test, a parametric test for pairwise comparisons of means (Sokol and Rohlf 1981), was performed to identify differences among specific data sets. Correlations were examined using Pearson product-moment correlations for pairs of variables (Sokol and Rohlf 1981).

Table 2. Acceptable data for metals analysis of water and laboratory method detection limits (mg/L). R indicates unacceptable data (poor spike or standard reference material recovery, poor precision within the zone of quantitation, and/or unacceptable levels of blank contamination). NA indicates that 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.

Analyte	Method[a]	1985	1987	1988
Aluminum	ICPP	NA	R	TM[b] 0.05
Antimony	ICPP	R	NA	R
Arsenic	AA	All 0.0005	TRM, DM 0.004	TM 0.003
Barium	ICPP	NA	NA	R
Beryllium	ICPP	NA	R	R
Boron	ICPP	NA	NA	R
Cadmium	ICPP	All 0.0001	TM, TRM[c] 0.0008	R
Chromium	ICPP	NA	TRM, DM 0.022	R
Cobalt	ICPP	NA	TM 0.002	NA
Copper	ICPP	All 0.0009	TRM, DM 0.0096	R
Iron	ICPP	All 0.0200	TRM, DM 0.101	TM 0.015
Lead	ICPP	All 0.001	All 0.012	DM 0.015[d]
Manganese	ICPP	All 0.0001	TRM, DM 0.0046	TM, TRM 0.01
Molybdenum	ICPP	NA	NA	R
Nickel	ICPP	All 0.001	TM, TRM[c] 0.005	TRM, DM 0.01
Selenium	AA	NA	NA	TM, DM 0.0025
Thallium	ICPP	NA	TRM, DM 0.05	All 0.05
Tin	ICPP	NA	DM 0.01	R
Vanadium	ICPP	NA	NA	R
Zinc	ICPP	All 0.01	TRM, DM[c] 0.0098	R

[a] ICPP = Inductively Coupled Argon Plasma analysis with preconcentration; AA = atomic absorption.

[b] TM = total metals analysis; TRM = total recoverable metals analysis; DM = dissolved metals analysis; All = TM, TRM and DM.

[c] TRM Quantitative Data.

[d] Analyzed using AA.

Table 3. Acceptable data for metals analysis of sediments showing laboratory method detection limits (mg/kg dry weight). R indicates unacceptable data (poor spike or standard reference material recovery, poor precision within the zone of quantitation, and/or unacceptable levels of blank contamination). NA indicates that 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.

Analyte	Method[a]	1985	1987	1988
Aluminum	ICP	NA	R	R
Antimony	ICP	R	R	R
Arsenic	AA	2.0	0.8	R
Beryllium	ICP	NA	0.1	0.1
Boron	ICP	NA	NA	R
Cadmium	ICP	0.05	0.5	0.5
Chromium	ICP	NA	0.3	R
Copper	ICP	3.0	R	0.5
Iron	ICP	10.0	R	R
Lead	ICP	2.0	5.0	5.0[b]
Magnesium	ICP		R	R
Manganese	ICP	10.0	0.54	R
Mercury	AA	0.02	0.2	1.0
Molybdenum	ICP	NA	2.0	1.0
Nickel	ICP	R	R	2.0
Selenium	AA	NA	NA	R
Thallium	ICP	NA	50.0	1.00
Tin	ICP	NA	50.0	10.0
Vanadium	ICP	NA	R	1.0
Zinc	ICP	15.0	R	R

[a] ICP = Inductively Coupled Argon Plasma analysis; AA = atomic absorption spectrophotometry.

[b] Analyzed using AA.

Table 4. Acceptable data for metals analysis of fish tissues showing laboratory method detection limits (mg/kg dry weight). R indicates unacceptable data (poor spike or standard reference material recovery, poor precision within the zone of quantitation, and/or unacceptable levels of blank contamination). NA indicates that 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.

Analyte	Method[a]	1985	1986/87	1988[b]	1989	1990
Aluminum	ICPP	R	R	55.0	3.0	7.38
Antimony	AA	NA	NA	30.0	NA	0.47[c]
Arsenic	AA	R	NA	0.2	6.0	NA
Barium	ICPP	NA	NA	1.0	0.2	3.69
Beryllium	ICPP	0.006	0.21	0.1	0.2	0.37
Boron	ICPP	NA	NA	0.5	2.0	0.5
Cadmium	ICPP	0.08	0.2	0.6	1.0	0.37
Chromium	ICPP	0.04	R	0.6	2.0	0.74
Cobalt	ICPP	R	R	3.0	NA	NA
Copper	ICPP	5.0	R	2.0	0.2	R
Iron	ICPP	10.0	R	30.0	1.0	7.38
Lead	ICPP	0.2	2.3	6.0[c]	4.0	0.47
Magnesium	ICPP	NA	NA	30.0	5.0	R
Manganese	ICPP	2.0	R	2.0	1.0	0.92
Mercury	AA	0.05	0.02	0.02	0.05	0.111
Molybdenum	ICPP	NA	NA	10.0	1.0	3.69
Nickel	ICPP	0.1	0.8	3.5	3.0	2.98
Selenium	AA	NA	NA	0.3	8.0[b]	NA
Silver	ICPP	NA	NA	9.0	2.0	3.69
Strontium	ICPP	NA	NA	3.0	R	0.74
Thallium	ICPP	0.7	NA	NA	4.0	14.8
Tin	ICPP	NA	R	R	NA	3.69
Vanadium	ICPP	NA	NA	0.5	1.0	3.69
Zinc	ICPP	R	R	15.0	R	1.47

[a] ICPP = Inductively Coupled Argon Plasma analysis with preconcentration; AA = atomic absorption spectrophotometry. [b] ICP without preconcentration. [c] Analyzed using AA.

Table 5. Estimated 95% confidence intervals (%) for ICPP and AA analyses, 1987, 1988, 1989, and 1990.

	ICP			AA		
Sample Concentration	0-2 X LOD[a]	2-10 X LOD	>10 X LOD	0-2 X LOD	2-10 X LOD	> 10 X LOD
1987	± 200	± 40	± 20	± 200	± 10	INS[b]
1988 Tissue, Sediment	± 200	± 30	± 10	± 200	± 20 Tiss. ± 25 Sed.	± 15
1989 Tissue	± 200	± 20	± 5	± 200	± 20	± 5
1990 Hair	± 200	± 30	± 10	± 200	± 25	± 15

[a] Limit of Detection.

[b] Insufficient data to estimate 95% confidence interval.

RESULTS

Water Quality

Water quality data are presented in Table 6. These data were collected May through August 1985-1990. Samples from major tributaries to the South Fork Koyukuk River including Bonanza (Site 30), Fish (Sites 6, 8, and 29) and Prospect (Site 33) creeks, and the Jim River (Sites 13 and 35) generally had low conductivity, hardness, and alkalinity values (<50 µS/cm, <25 mg/L, and <15 mg/L, respectively). Values of pH for samples from these sites ranged from 6.25 to 8.25. All settleable solids measurements were either none or trace. Turbidity measurements from samples taken at these sites were up to 9 NTU. All conductivity, hardness, and alkalinity values measured from samples taken from the South Fork Koyukuk River (Sites 3, 5, 7, 9, 10, 11, and 12) were greater than those measured on tributary streams. Conductivity values ranged from 52 µS/cm to 175 µS/cm, hardness values ranged from 28 mg/L to 100 mg/L, and alkalinity values ranged from 20 mg/L to 40 mg/L. During a 4-day period in May 1987, samples from South Fork Koyukuk River Sites 3, 5, 7, 10, 11, and 12 were similar in conductivity, hardness, and alkalinity. Samples from more upstream sites (Sites 10, 11, and 12) had the highest values of these variables. Values of pH in South Fork Koyukuk River samples ranged from 6.89 to 8.4. All settleable solids measurements, except one at Site 5, were either none or trace. Turbidity measurements at these sites were up to 36 NTU.

Samples from tributaries to the Middle Fork Koyukuk River, including Marion (Site 39), Minnie (Site 45), Rosie (Site 46), and Slate (Site 47) creeks, sampled on 14 June 1990, had conductivity values ranging from 108 µS/cm to 168 µS/cm, and hardness values from 49 mg/L to 83 mg/L; both were higher than those for the major tributaries of the South Fork Koyukuk River (Table 6). Values of pH at these sites ranged from 8.1 to 8.65. Conductivity, hardness, and alkalinity values of Middle Fork Koyukuk River samples (Sites 23, 24, 25, 26, and 40) were the highest measured during this study. On 23 August 1988, during a high-water period due to rain, the mean conductivity values from samples taken at Sites 23, 24, 25, and 26 ranged from 377 µS/cm to 693 µS/cm, mean hardness values ranged from 192 mg/L to 271 mg/L, and mean alkalinity values ranged from 90 mg/L to 145 mg/L. Mean pH values from samples at these sites ranged from 8.14 to 8.32. Samples from Site 24, located on the Middle Fork Koyukuk River just below its confluence with the Hammond River, had the highest mean values of conductivity, hardness, alkalinity, and pH. Settleable solids measurements at Middle Fork Koyukuk River sites were trace, and mean turbidity values ranged from 23 NTU to 60 NTU, higher than in samples from the South Fork Koyukuk River and its tributaries.

Replicate analyses from Sites 2 and 20 (Koyukuk R.), 22 (Wild R.), and 23, 24, 25 and 26 (Middle Fork Koyukuk R.) were performed, thus allowing statistical analysis. Using the ANOVA test, numerous statistical differences ($P < 0.05$) occurred between sample sites for water quality variables (Table 7). In addition, alkalinity values from samples at these sites were highly correlated with conductivity ($r^2 = 0.91$, df = 20, $P < 0.01$) and pH ($r^2 = 0.83$, df = 20, $P < 0.01$). Conductivity was also highly correlated with pH ($r^2 = 0.84$, df = 20, $P < 0.01$).

Table 6. Water quality data collected during 1985, and 1987-1990 at Kanuti National Wildlife Refuge, Alaska. Sites are ordered by major drainage followed by tributaries of the major drainage. Blanks indicate that no data were collected.

Site	Site #	Date	Cond.[a] µS/cm	pH	Sus. S.[b] mg/L	S.S.[c] mL/L	Turb.[d] NTU	Hard.[e] mg/L	Alk.[f] mg/L
South Fork Koyukuk River	3	06/25/85	88	7.43		Trace	23	39	34
South Fork Koyukuk River	3	08/19/85	80	7.61			6	32	28
South Fork Koyukuk River	3	05/26/87	54	6.76	41	Trace	36	28	21
South Fork Koyukuk River	3	07/06/89	97	8.2	25	Trace	2	100	40
South Fork Koyukuk River	5	06/26/85	96	7.56		Trace	21	40	28
South Fork Koyukuk River	5	08/20/85		7.60		None	3	43	35
South Fork Koyukuk River	5	05/27/87	67	6.80	85	0.2	17	32	26
South Fork Koyukuk River	5	07/06/89	52	8.23	8.3	Trace	4	42	20
South Fork Koyukuk River	7	06/26/85	90	7.60			18	37	25
South Fork Koyukuk River	7	05/26/87	65	6.96	435	Trace	14	34	26
South Fork Koyukuk River	9	06/14/90	175	8.4		None	2	86	
South Fork Koyukuk River	10	05/28/87	78	6.89	10	Trace	4	39	31
South Fork Koyukuk River	11	05/28/87	81	6.91	9	Trace	4	40	32
South Fork Koyukuk River	12	05/29/87	90	7.09	14	Trace	9	49	36
Fish Creek	6	08/20/85	43	6.93		None	3	14	9
Fish Creek	6	05/27/87	34	6.25	26	Trace	9	13	9
Fish Creek	6	07/06/89	120	8.09	2.8	Trace	6	66	46
Fish Creek	8	06/27/85	50	7.30			5	15	7
Fish Creek	29	06/13/90	27	8.5		Trace	1	10	
Bonanza Creek	30	06/13/90	35	7.8		None	1	13	
Jim River	13	05/29/87	40	6.59	5	Trace	6	21	14
Jim River	35	06/15/90	35	8.15		None	1	17	

Table 6 Cont.

Site	Site #	Date	Cond. µS/cm	pH	Sus. S mg/L	S.S. mL/L	Turb. NTU	Hard. mg/L	Alk. mg/L
Prospect Creek	33	06/13/90	72	7.85		None	1	30	
Middle Fork Koyukuk River	23[g]	08/23/88	377	8.14	36	Trace	33	199	90
Middle Fork Koyukuk River	24[g]	08/28/88	693	8.32	23	Trace	22	271	145
Middle Fork Koyukuk River	25[g]	09/01/88	557	8.28	60	Trace	48	194	139
Middle Fork Koyukuk River	26[g]	09/05/88	565	8.28	47	Trace	51	192	141
Middle Fork Koyukuk River	40	06/14/90	550	8.53		Trace	34	206	
Rosie Creek	39	06/14/90	130	8.35		None	3.1	58	
Slate Creek	45	06/14/90	108	8.25		None	2	49	
Marion Creek	46	06/14/90	154	8.1		None	0.6	68	
Minnie Creek	47	06/14/90	168	8.65		None	2	83	
Koyukuk River	1	06/24/85	290	8.13		Trace	73	130	66
Koyukuk River	1	08/18/85	360	8.00		None	3	171	95
Koyukuk River	1	05/25/87	160	7.58	90	Trace	56	88	57
Koyukuk River	1	07/06/89	360	7.69	26	Trace	13	174	93
Koyukuk River	2	06/25/85	260	8.01			353	129	68
Koyukuk River	2	05/26/87	155	7.52	166	0.1	75	79	56
Koyukuk River	2[g]	08/22/88	338	7.93	130	Trace	81	174	90
Koyukuk River	2	07/06/89	300	7.57	26	Trace	17	180	89
Koyukuk River	4	06/25/85	240	8.28		0.3	350	115	69
Koyukuk River	4	08/19/85	360	8.05		None		172	98
Koyukuk River	4	05/26/87	152	7.47	139	1.7	85	78	54
Koyukuk River	4	07/06/89	295	8.15	6	Trace	12	171	90
Henshaw Creek	19	07/06/89	93	7.42	4.9	Trace	18	74	44
John River	20	07/06/89	285	7.92	18	Trace	14	144	79
John River	20[g]	08/22/88	342	7.99	126	Trace	111	160	90
Wild River	22		275	7.9	1.1	Trace	1.1	146	112
Wild River	22[g]	08/22/88	240	7.98	23	Trace	4	154	86

Table 6 continued

Site	Site #	Date	Cond. µS/cm	pH	Sus. S. mg/L	S.S. mL/L	Turb. NTU	Hard. mg/L	Alk. mg/L
Kanuti River	15	07/06/89	82	7.01	4.4	Trace	6.2	41	34
Kanuti-Kilolitna River	17	07/06/89	68	7.15	4.4	Trace	4.2	20	27
Kanuti River	43	07/06/89	92	6.92	30	Trace	7.6	46	40

[a] Conductivity. [b] Suspended solids. [c] Settleable solids. [d] Turbidity. [e] Hardness. [f] Alkalinity.
[g] Values are the mean of three sample replicates.

Samples from Henshaw Creek (Site 19), a tributary of the Koyukuk River, had conductivity, hardness, and alkalinity values of 93 µS/cm, 74 mg/L, and 44 mg/L, respectively. The single pH measurement at this site was 7.42 on 6 July 1989. Samples from the John and Wild rivers, also tributaries of the Koyukuk River, had similar conductivity, hardness, alkalinity, pH, and settleable solids values on 22 August 1988 (Table 6). John River samples had much higher turbidity and suspended solids values than those from the Wild River. Conductivity, hardness and alkalinity values on samples taken from the Koyukuk River (Sites 1, 2, and, 4) were generally greater than those from samples of the South Fork Koyukuk River and less than those of Middle Fork Koyukuk River samples (Table 6). Conductivity measurements of Koyukuk River samples ranged from 152 µS/cm to 360 µS/cm. Hardness values ranged from 78 mg/L to 180 mg/L, and alkalinity values ranged from 54 mg/L to 98 mg/L (Table 6). Values of these variables at Sites 1, 2, and 4 were very similar on each of several sample periods. Values of pH for Koyukuk River samples ranged from 7.42 to 8.28, generally less than the pH of Middle Fork Koyukuk River samples and greater than those taken from the South Fork Koyukuk River. Settleable solids measurements from Koyukuk River samples ranged from none detected to 1.7 mL/L. Turbidity measurements ranged from 3 NTU to 353 NTU, and suspended solids measurements ranged from 5 mg/L to 166 mg/L. Suspended and settleable solids measurements were generally greater in Koyukuk River samples than those taken at Middle Fork and South Fork Koyukuk River sites.

Trace Elements

Water

Total Metals. 1985 - All sites sampled during 1985 were on either the Koyukuk River (Sites 1, 2 and 4), or the South Fork Koyukuk River (Sites 3, 5, and 7) or its tributary, Fish Creek (Sites 6 and 8). QA-QC screening indicates that arsenic, cadmium, copper, iron, lead, manganese, nickel, and zinc data are acceptable from 1985 samples (Table 8). Cadmium was detected in two of six samples near the LOD. Arsenic, copper, iron, lead, manganese, and nickel were detected in each sample. Zinc was detected in three of six samples. There was an insufficient sample size to make statistical comparisons between metals concentrations of the Koyukuk and South Fork Koyukuk rivers. In general, concentrations of metals, except cadmium and lead, were slightly higher in Koyukuk River samples than in those from the South Fork Koyukuk River. Mean values of copper, iron, manganese, and nickel were an order of magnitude greater in Koyukuk River samples than in those from the South Fork Koyukuk River. Samples from Sites 2 and 4 had the highest and second highest concentration of all metals, respectively.

When data from all sites sampled during 1985 were pooled, turbidity was significantly correlated with concentrations of copper ($r^2 = 0.90$, df = 5, $P < 0.05$), iron ($r^2 = 0.90$, df = 5, $P < 0.05$), manganese ($r^2 = 0.95$, df = 5, $P < 0.001$), nickel ($r^2 = 0.87$, df = 5, $P < 0.05$), and zinc ($r^2 = 0.83$,

Table 7. Scheffe' groupings expressing significant differences among seven water quality sampling sites at Kanuti National Wildlife Refuge, Alaska, 22 August 1988. Sample sites that contain the same letter did not have significantly different values.

Site	Conductivity	pH	Suspended Solids	Turbidity	Hardness	Alkalinity
2-Koyukuk R.	B	A	C	EF	AB	AB
20-John R.	B	A	BC	F	A	AB
22-Wild R.	A	A	A	A	A	A
23 MF-Koyukuk R.	B	B	AB	BC	AB	AB
24 MF-Koyukuk R.	C	C	A	AB	B	C
25 MF-Koyukuk R.	B	C	ABC	CD	AB	BC
26 MF-Koyukuk R.	B	C	ABC	DE	AB	C

df = 5, $P < 0.05$). Alkalinity was significantly correlated with lead concentrations ($r^2 = 0.84$, df = 5, $P < 0.05$). Arsenic concentrations were not significantly correlated with any water quality parameters.

1987 - All sites sampled during 1987 were on either the Koyukuk River (Sites 1, 2, and 4), or the South Fork Koyukuk River (Sites 3, 5, 7, 10, 11, 12, and 13) or its tributary, Fish Creek (Site 6). QA-QC screening indicates that for two of the three replicate samples arsenic, cadmium, chromium, copper, iron, lead, manganese, nickel, thallium, and zinc data are acceptable (Table 9, Appendix E). The third replicate samples were analyzed separately. QA-QC screening indicates that from these analyses, cadmium, cobalt, lead, and nickel data are acceptable. Total cadmium was detected in only one sample. Arsenic, chromium, and thallium were not detected. Copper was detected in every sample but one, and total iron, manganese, nickel, and zinc were detected in each sample. The two total lead analyses differed. In one analysis, lead was not detected at an LOD of 0.012 mg/L and in the other, lead was detected in each sample in concentrations exceeding 0.012 mg/L. Analytical error is the suspected cause of this discrepancy and there is no way of determining which values are correct. Duplicate analyses for both sets of analyses were <2(LOD) and these data should be considered semi-quantitative (Table 9). There were insufficient acceptable sample analyses to allow statistical comparisons between metals concentrations in water samples from the Koyukuk and South Fork Koyukuk rivers. Except for lead, concentrations of metals were slightly higher in the Koyukuk River than in the South Fork Koyukuk River.

Examination of total water analyses from all 1987 samples showed several significant differences in metal concentrations among sample sites. Samples from Site 4 (Koyukuk River) had significantly greater concentrations of iron ($F_{6,7} = 9.94$, $P < 0.05$) than those taken at Site 10 (South Fork Koyukuk River), and significantly greater concentrations of copper ($F_{6,7} = 6.92$, $P < 0.05$), iron ($F_{6,7} = 9.94$, $P < 0.05$) and manganese ($F_{6,7} = 6.92$, $P < 0.05$) than samples from Site 11 (South Fork Koyukuk River). Concentrations of copper, iron, lead, manganese, and nickel were not highly correlated with water quality variables.

1988 - Water samples collected during 1988 were from the Middle Fork Koyukuk River (Sites 23, 24, 25, and 26), Koyukuk River (Site 2), John River (20), and Wild River (Site 22). QA-QC screening indicates that aluminum, arsenic, iron, manganese, selenium, and thallium data are acceptable (Table 10). Aluminum, iron, and manganese were detected in each sample at

Table 8. Total, total recoverable, and dissolved metal concentrations in water from Kanuti National Wildlife Refuge, Alaska, 1985.

			Metal Concentrations (mg/L)							
Site	Sample	Date	As	Cd	Cu	Fe	Pb	Mn	Ni	Zn
1	T[a]	06/24	0.0006	<0.0001	0.009	5.70	0.007	0.150	0.010	0.030
2	T	06/25	0.0095	0.0002	0.031	30.00	0.010	0.460	0.031	0.087
3	T	06/25	0.0006	<0.0001	0.004	1.90	0.002	0.039	0.005	<0.01
4	T	06/25	0.0032	0.0001	0.020	18.00	0.007	0.350	0.019	0.049
5	T	06/26	0.0026	<0.0001	0.003	1.80	0.002	0.052	0.002	<0.01
7	T	06/26	0.0005	<0.0001	0.002	1.20	0.003	0.043	0.003	<0.01
1	R[b]	08/18	<0.0005	<0.0001	0.001	0.34	<0.001	0.016	0.003	<0.01
2	R	08/19	0.0010	<0.0001	0.001	0.27	0.002	0.013	0.002	<0.01
3	R	08/19	0.0010	<0.0001	0.002	1.40	0.003	0.047	0.002	<0.01
4	R	08/19	0.0005	<0.0001	0.001	0.32	0.002	0.022	0.001	<0.01
5	R	08/20	0.0010	<0.0001	0.001	0.38	0.003	0.017	0.002	<0.01
6	R	08/20	0.0006	<0.0001	0.002	0.59	<0.001	0.025	0.002	<0.01
8	R	08/20	0.0010	<0.0001	0.002	0.51	0.002	0.023	0.002	<0.01
1	D[c]	06/24	<0.0005	<0.0001	0.003	0.02	<0.001	0.011	0.004	<0.01
2	D	06/25	<0.0005	*[d]	0.006	0.06	0.003	0.009	0.002	<0.01
3	D	06/25	<0.0005	<0.0001	*[d]	0.23	0.002	0.013	0.002	<0.01
4	D	06/25	0.0005	<0.0001	0.005	0.20	<0.001	0.013	0.003	<0.01
5	D	06/26	0.0006	<0.0001	*[d]	0.22	<0.001	0.020	*[d]	<0.01
7	D	06/26	0.0005	<0.0001	0.002	0.13	0.002	0.012	*[d]	0.010

[a] Total metals analysis. [b] Total recoverable metals analysis. [c] Dissolved metals analysis.
[d] Result was greater than the total metals analysis.

Table 9. Mean total, total recoverable, and dissolved metal concentrations in water from Kanuti National Wildlife Refuge, Alaska, 1987.

			Metals Concentrations (mg/L)					
Site	Sample[a]	n	Cu	Fe	Pb	Mn	Ni	Zn
1	T	2	0.012	4.65	0.050	0.146	0.008	0.024
2	T	2	0.013	6.72	0.022	0.167	0.064	0.027
3	T	2	0.008	2.58	0.058	0.079	0.006	0.015
4	T	2	0.014	6.67	0.042	0.170	0.012	0.026
5	T	1	0.011	5.57	0.037	0.122	0.009	0.020
6	T	2	0.005	1.62	0.025	0.037	0.005	0.012
7	T	1	<0.007[b]	1.81	0.034	0.054	0.005	0.016
10	T	2	0.007	0.68	0.032	0.033	0.005	0.010
11	T	2	0.003	0.53	0.032	0.026	0.008	0.010
12	T	1	0.009	1.17	0.032	0.041	0.004	0.011
13	T	1	0.008	0.54	0.057	0.020	0.004	0.007
1	R	2	-[c]	4.10	0.026	0.133[d]	0.007[d]	0.019
2	R	2	0.008	7.16[d]	0.015	0.197[d]	0.017[d]	0.025
3	R	2	<0.007	2.51	0.024	0.075	*[e]	0.007
4	R	2	-	6.48	0.028	0.160	0.009[d]	0.018
5	R	1	<0.007	4.96	0.023	0.115	*	0.018
6	R	2	<0.007	1.51	0.014	0.035	<0.003[d]	0.007
7	R	1	<0.007	1.79	0.024	0.053	*	0.012
10	R	2	<0.007	0.61[d]	0.024	0.031[d]	0.004[d]	0.006
11	R	2	<0.007	0.072[d]	0.024	0.027[d]	*	<0.001
12	R	1	*	*	*	*	*	*
13	R	1	<0.007	0.55	0.022	0.018	<0.003	<0.01
1	D	3	<0.007	0.15	*	0.030	QA[f]	0.017
2	D	3	-	0.15	*	0.022	QA	0.011
3	D	3	<0.007	0.33	*	0.021	QA	-
4	D	3	<0.007	0.18	*	0.019	QA	-

Table 9 continued

Site	Sample	n	Cu	Fe	Pb	Mn	Ni	Zn
5	D	3	<0.007	0.29	*	0.017	QA	0.013
6	D	3	<0.007	0.69	*	0.029	QA	-
7	D	3	<0.007	0.23	*	0.014	QA	0.011
10	D	3	-	0.14	*	0.010	QA	-
11	D	3	<0.007	0.11	*	0.010	QA	-
12	D	3	<0.007	0.11	*	0.010	QA	-
13	D	3	<0.007	0.32	*	0.013	QA	0.112

[a] T = Total metals, R = total recoverable metals, and D = dissolved metals.
[b] All analyses were <LOD.
[c] Dash (-) indicates that ≥50% of the analyses were <LOD.
[d] One of the two replicate analyses was greater than the total metals analysis and was discarded.
[e] Asterisk (*) indicates that result was greater than the total metals analysis.
[f] Did not pass QA screening.

concentrations up to 2.92 mg/L, 6.94 mg/L, and 0.13 mg/L, respectively. Arsenic and selenium were not detected in any sample. In general, samples from Site 22 (Wild River) had the lowest total metal concentrations and those from Sites 2 and 20 (Koyukuk River) had the highest.

Examination of the pooled 1988 analyses showed that turbidity and suspended solids were highly correlated with concentrations of aluminum ($r^2 = 0.88$, df = 19, $P < 0.01$) ($r^2 < 0.87$, df = 19, $P < 0.01$), iron ($r^2 = 0.90$, df = 19, $P < 0.01$) ($r^2 = 0.92$, df = 19, $P < 0.01$), and manganese ($r^2 = 0.80$, df = 19, $P = 0.01$) ($r^2 = 0.84$, df = 19, $P = 0.01$), respectively.

Total Recoverable Metals. 1985 - QA-QC screening indicates that arsenic, cadmium, copper, iron, lead, manganese, nickel, and zinc data are acceptable (Table 8). Arsenic was detected in five of six samples in concentrations up to 0.001 mg/L. Cadmium and zinc were not detected in any sample. Copper, iron, manganese, and nickel were detected in each sample.

When data from all sites were pooled, concentrations of arsenic, copper, iron, lead, manganese, and nickel were not highly correlated with water quality variables. Iron and manganese concentrations were slightly higher from samples taken in the South Fork Koyukuk River drainage, including Fish Creek, than from samples collected at Koyukuk River sites. All other metals concentrations from samples in the two river systems were low and similar to one another.

1987 - QA-QC screening indicates that arsenic, cadmium, chromium, copper, and lead data are acceptable from 1987 samples (Table 9, Appendix E). Arsenic and thallium were not detected in any sample. Data for cadmium and chromium were greater than those for total metals analyses and were discarded. Iron, manganese, nickel, and zinc were detected in all samples. Some of these results were greater than those for the corresponding total metals analysis and were discarded (Table 9). Mean iron, manganese, and zinc concentrations were higher in samples from the Koyukuk River than in those collected on the South Fork Koyukuk River, Fish Creek, and Jim River.

Examination of combined total recoverable water analyses from 1987 showed several significant differences in metal concentrations among sample sites. Samples collected at Sites 2 and 4 (Koyukuk River) had significantly greater concentrations of iron ($F_{6,7} = 15.19$, $P < 0.01$) than

Table 10. Total metal concentrations in water from Kanuti National Wildlife Refuge, Alaska, 1988.

			Metals Concentrations (mg/L)			
Site	Replicate	Date	Al	Fe	Mn	Tl
2	A	08/22	2.73	6.94	0.13	<0.05
2	B	08/22	2.92	6.42	0.12	<0.05
2	C	08/22	2.49	6.29	0.13	0.02
Mean			2.71	6.55	0.13	[a]
20	A	08/22	2.50	6.06	0.11	0.02
20	B	08/22	2.63	6.52	0.12	<0.05
20	C	08/22	2.77	6.43	0.11	<0.05
Mean			2.63	6.34	0.12	
22	A	08/22	0.19	0.39	0.02	0.02
22	B	08/22	0.06	0.38	0.03	<0.05
22	C	08/22	0.19	0.40	0.03	<0.05
Mean			0.15	0.39	0.03	
23	A	08/23	1.32	2.94	0.09	<0.05
23	B	08/23	0.99	2.18	0.07	<0.05
23	C	08/23	0.54	1.31	0.04	<0.05
Mean			0.95	2.14	0.07	<0.05
24	A	08/23	0.66	1.18	0.06	<0.05
24	B	08/23	0.50	1.14	0.06	<0.05
24	C	08/23	0.71	1.15	0.06	<0.05
Mean			0.63	1.16	0.06	<0.05

Table 10 Cont.

Site	Rep.	Date	Al	Fe	Mn	Tl
25	A	08/23	1.43	3.27	0.09	<0.05
25	B	08/23	1.51	3.13	0.08	<0.05
25	C	08/23	1.53	3.36	0.09	<0.05
Mean			1.49	3.25	0.08	<0.05
26	A	08/23	1.00	2.48	0.06	<0.05
26	B	08/23	1.03	2.48	0.06	<0.05
26	C	08/23	1.66	2.87	0.07	0.03
Mean			1.23	2.61	0.06	

[a] Mean values are not calculated when greater than one-half of the values are <LOD.

those taken at Sites 6 (Fish Creek), 10, and 11 (South Fork Koyukuk River). Site 2 samples also had significantly greater concentrations of zinc ($F_{6,7} = 15.74$, $P < 0.01$) than those collected at Sites 3 (South Fork Koyukuk River), 6, 10, and 11. No metals concentrations were significantly correlated with water quality variables.

1988 - QA-QC screening indicates that arsenic, manganese, nickel, and thallium data are acceptable from 1988 samples (Appendix F). Arsenic was not detected except in concentrations greater than the corresponding total metals analysis. Manganese was detected at each site in concentrations as high as 0.09 mg/L; however, many detections were greater than the corresponding total metals analysis. Nickel was detected only at Site 2 and near the LOD. Thallium was not detected.

Manganese concentrations from samples collected at Sites 2 and 20 (Koyukuk River) were significantly greater ($F_{6,14} = 26.14$, $P < 0.01$) than those from samples at Site 22 (Wild River), and samples collected at Sites 23, 24, and 26 (Middle Fork Koyukuk River). Manganese concentrations of samples collected at Sites 24 and 25 (Middle Fork Koyukuk River) were significantly greater ($F_{6,14} = 26.37$, $P < 0.01$) than at Site 22. Manganese concentrations were not correlated with any water quality variables.

Dissolved Metals 1985 - QA-QC screening indicates that arsenic, cadmium, copper, iron, lead, manganese, nickel, and zinc data are acceptable (Table 8). Arsenic was detected in three of six samples, all near the LOD. Cadmium was detected at one site; however this value is slightly greater than that of the total cadmium concentration at this site and was discarded. Copper, iron, manganese, and nickel were detected in each sample. Very little difference occurred between sample sites for these parameters. Concentrations of arsenic, copper, iron, lead, manganese, and nickel were not highly correlated with water quality variables.

1987 - QA-QC screening indicates that arsenic, chromium, copper, iron, lead, manganese, tin, thallium, and zinc data are acceptable from 1987 samples (Table 9, Appendix E). Arsenic, chromium, copper, and thallium were not detected in any sample. Iron was detected in 27 of 31 samples at concentrations up to 1.060 mg/L. Dissolved lead values were greater than the total lead values and were discarded. Manganese was detected in each sample in concentrations up to 0.039 mg/L. Tin was detected in two of three replicate samples at one site, Site 3 (South Fork Koyukuk River), with a mean of 0.16 mg/L. Zinc was detected at all 1987 sites, except Site 12 (South Fork Koyukuk River), in concentrations up to 0.313 mg/L. The mean values of iron, manganese, and zinc were higher in samples collected on Fish Creek than in those taken on all other waterbodies during 1987.

Examination of 1987 analysis for dissolved metals in water showed several significant differences in metal concentrations among sample sites. Site 6 (Fish Creek) samples had significantly greater concentrations of iron ($F_{10,22} = 4.5$, $P < 0.01$) than in those from Sites 1, 2 (Koyukuk River), 10, 11, and 12 (South Fork Koyukuk River). Site 1 had significantly greater concentrations of manganese ($F_{10,22} = 6.1$, $P < 0.01$) than in samples collected at Sites 10, 11, and 12. Metals concentrations were not highly correlated with one another or with water quality variables.

1988 - QA-QC screening indicates that lead, nickel, selenium, and thallium data are acceptable (Appendix F). Lead was detected in each sample with one exception at concentrations up to 0.06 mg/L. Nickel, thallium and selenium were not detected in any sample. Lead concentrations were not highly correlated with water quality variables and did not differ significantly among sites.

Sediment

1985 - QA-QC screening indicates that arsenic, cadmium, copper, iron, lead, manganese, mercury, and zinc are acceptable from 1985 samples (Table 11). SRM recoveries for nickel were slightly lower than the standard and indicate that values for this variable are likely low. Arsenic, copper, iron, manganese, nickel, and zinc were detected in each sample, but concentrations were generally low. Cadmium was detected in all but one sample and all concentrations were < 0.45 mg/kg. Mercury was detected only at the LOD (0.05 mg/kg); these results should be considered semi-quantitative. Samples from Site 1 (Koyukuk River) had the highest concentrations of metals, except for cadmium and lead. Samples from Sites 1, 2, and 4 (Koyukuk River) had slightly higher mean concentrations of copper, iron, lead, manganese, and nickel than from samples collected at Sites 3, 5, 7, 8, and 9 (South Fork Koyukuk River).

When all 1985 data were pooled, several highly significant correlations among metal concentrations were found. Manganese was significantly correlated with arsenic ($r^2 = 0.82$, df = 8, $P < 0.01$), iron ($r^2 = 0.84$, df = 8, $P < 0.01$), nickel ($r^2 = 0.88$, df = 8, $P < 0.01$), and zinc ($r^2 = 0.88$, df = 8, $P < 0.01$). Zinc was significantly correlated with iron ($r^2 = 0.93$, df = 8, $P = 0.01$) and nickel ($r^2 = 0.89$, df = 8, $P < 0.01$), and iron was significantly correlated with nickel ($r^2 = 0.93$, df = 8, $P < 0.01$). Conductivity was significantly correlated with copper concentrations ($r^2 = 0.84$, df = 5, $P < 0.01$).

1987 - QA-QC screening indicates that arsenic, barium, beryllium, cadmium, chromium, lead, manganese, mercury, molybdenum, strontium, tin, and thallium were acceptable from 1987 samples (Table 12, Appendix G). SRM recoveries for copper and nickel were low indicating that the sample concentrations reported are likely low. Conversely, SRM recoveries for zinc were slightly higher than the standard indicating that concentrations reported for this variable may be slightly high. Arsenic, barium, chromium, manganese, nickel, strontium, and zinc were detected in each sample. Mercury was detected in only 4 of 33 samples (one concentration above the LOD each was detected at Sites 1, 2, 10, and 11), all near the LOD. Copper and zinc concentrations from samples collected at Site 1 (Koyukuk River) were significantly greater (Cu: $F_{10,22} = 4.3$, $P < 0.01$; Zn: $F_{10,22} = 5.1$, $P < 0.01$) than samples taken at Sites 3 and 5 (South Fork Koyukuk River). Nickel concentrations from samples collected at Site 1 were significantly

greater ($F_{10,22} = 4.10$, $P < 0.01$) than those collected at Site 3, and manganese concentrations from Site 1 samples were significantly greater ($F_{10,22} = 5.72$, $P < 0.01$) than those taken at Sites 5, 6 (Fish Creek), and 11 (South Fork Koyukuk River). Barium concentrations from samples collected at Site 4 (Koyukuk River) were significantly less ($F_{10,22} = 5.66$, $P < 0.01$) than in samples collected at Site 13 (Jim River), and lead concentrations from Site 4 samples were significantly greater ($F_{10,22} = 6.82$, $P < 0.01$) than those taken at Sites 3, 5, 7 (South Fork Koyukuk River), and 13. Using pooled data, copper was significantly correlated with nickel ($r^2 = 0.84$, df = 32, $P < 0.01$) and zinc ($r^2 = 0.80$, df = 32, $P < 0.01$). No water quality variables were significantly correlated with metal concentrations.
1988 - QA-QC screening indicates that arsenic, barium, beryllium, cadmium, copper, iron, lead, mercury, molybdenum, nickel, selenium, strontium, tin, thallium, and vanadium data were acceptable from 1988 samples (Table 13, Appendix H). Spiked recoveries for zinc were low indicating that concentrations reported may be lower than the actual concentrations. Cadmium was detected in at least one of three replicate samples at each sample site except Site 26 (Middle Fork Koyukuk River). Mercury and selenium were not detected in any samples. Molybdenum was detected in four samples, all at the LOD. All other metals for which analyses were conducted were detected in each sample. Site 22 (Wild River) samples had either the highest or second highest mean values for all metals except tin. Mean arsenic, copper, lead, manganese, nickel, strontium, and zinc concentrations were greater in Koyukuk River samples than in those collected on the South Fork Koyukuk River.

Beryllium, cadmium, and tin concentrations did not differ among sample sites. All other mean metal concentrations differed significantly among sites (Table 14). Nickel and iron concentrations were significantly correlated ($r^2 = 0.81$, df = 20, $P < 0.01$) as were copper and vanadium concentrations ($r^2 = 0.84$, df = 20, $P < 0.01$). No water quality variables were significantly correlated with metal concentrations.

Tissue

1985 - Twenty-eight samples were collected from 14 fish either from the South Fork Koyukuk River drainage or Site 1 (Koyukuk River) during 1985. QA-QC screening indicates that beryllium, cadmium, chromium, iron, lead, manganese, mercury, nickel, and thallium data were acceptable from 1985 samples (Table 15). The aluminum analyses had an Relative Percent Difference of 28%. However, several results for aluminum are an order of magnitude greater than the rest of the results, making a slight loss of precision inconsequential. Beryllium and thallium were not detected in any sample. Cadmium was detected in 9 (7 kidney, 2 liver) of 28 samples in concentrations up to 3.45 mg/kg and in kidney of each species at each sample site. Lead was detected in two kidney and one muscle sample in concentrations up to 1.83 mg/kg. Chromium was detected in at least one tissue from each fish except one whole body northern pike sample. Iron, manganese, and mercury were detected in all tissues. Mercury concentrations ranged between 4.07 mg/kg in a northern pike kidney to 0.15 mg/kg in a humpback whitefish liver. The northern pike from Site 5 had much higher mercury concentrations than any other fish.

1986 - Eleven samples were collected from 6 fish during 1986. QA-QC screening indicates that beryllium, cadmium, chromium, cobalt, lead, mercury, and nickel were acceptable from 1986 samples (Table 16). Beryllium and lead were not detected in any tissue. Cadmium and cobalt were detected in four samples each and chromium was detected in five samples; no pattern is evident from these data. Chromium and cobalt each had QA/QC spike recoveries of 78%, 2% lower than the standard, thus, reported concentrations may be slightly low. Mercury was detected in each sample; the highest concentration, 1.49 mg/kg, was in a northern pike.

1987 - During 1987, 105 samples were collected from 55 fish. QA-QC screening indicates that beryllium, cadmium, chromium, cobalt, lead, mercury, and nickel were acceptable from 1987 samples (Table 17, Appendix I). Beryllium and lead were detected in one and two samples, respectively. Cadmium, chromium, and nickel were detected in 40, 43, and 46 samples, respectively. Mean cadmium concentrations were highest in longnose sucker, up to 6.39 mg/kg. For longnose sucker and northern pike, cadmium concentrations were kidney >liver >muscle for all cases. Eleven of 17 measurable concentrations of cobalt were from Arctic grayling whole body samples, with concentrations up to 2.32 mg/kg. Chromium and cobalt each had QA-QC spike recoveries of 78%, 2% lower than the stated standard, thus, reported concentrations may be slightly low. Nickel was detected in concentrations up to 14.4 mg/kg. Nickel concentrations in specific tissues for longnose sucker followed the same pattern as for cadmium; however, nickel concentrations in northern pike muscle were higher than in liver. Mercury was detected in all tissues, in concentrations up to 2.28 mg/kg. For longnose sucker and northern pike, mercury concentrations in muscle were greater than those in liver tissue. For northern pike, mercury was also more concentrated in muscle than in kidney. Northern pike had greater concentrations of mercury than did longnose sucker. Metals concentrations from all sites were combined within tissue type and species for statistical comparison. For longnose sucker, cadmium concentrations in kidney were significantly greater ($F_{2,24} = 13.6$, $P < 0.01$) than in liver and muscle; mercury concentrations in muscle were significantly greater ($F_{2,15} = 9.0$, $P < 0.01$) than in liver; and nickel concentrations in kidney were significantly greater ($F_{2,24} = 5.5$, $P < 0.01$) than in muscle. For northern pike, cadmium concentrations in kidney were significantly greater ($F_{2,14} = 3.9$, $P < 0.05$) than in liver and muscle, and mercury concentrations in muscle were significantly greater ($F_{2,14} = 3.9$, $P < 0.05$) than in liver.

1988 - Fifty samples were collected from 22 fish during 1988. QA-QC screening indicates that aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, mercury, nickel, selenium, silver, strontium, vanadium, and zinc data were acceptable from 1988 samples (Table 18, Appendix J). Aluminum, antimony, molybdenum, and silver were not detected in any sample. Barium was detected in 11 samples, all <2(LOD), except for three whole Arctic grayling which had concentrations up to 4.0 mg/kg. Beryllium and cobalt were detected in seven and one samples, respectively; however, cobalt had a high LOD of 3.0 mg/kg. Beryllium was detected only in northern pike and longnose sucker in concentrations as high as 0.35 mg/kg in a longnose sucker liver. The range of mean cadmium concentrations was <0.60 - 49.03 mg/kg. Mean cadmium concentrations were highest at Site 1 (Koyukuk River), and higher in longnose sucker than in those measured in Arctic grayling and northern pike. Copper and lead were detected in almost all samples. Copper concentrations among tissues varied widely and were generally greatest in liver for all species. The range of copper concentrations was <2.00 - 65.20 mg/kg. Lead concentrations were generally greatest in Arctic grayling and lowest in northern pike, and ranged from <0.21 to 3.00 mg/kg. Magnesium, mercury, selenium, and zinc were detected in each sample. Mean magnesium concentrations ranged from 315 mg/kg to 1460 mg/kg and were highest in muscle for all species. Mean mercury concentrations ranged from 0.028 to 1.540 mg/kg, and were higher in Arctic grayling than in northern pike or longnose sucker. Selenium concentrations ranged from 1.25 to 22.70 mg/kg. Selenium concentrations in Arctic grayling kidney at Site 1 (Koyukuk River) and Arctic grayling liver at Site 22 (Wild River) were very high; both were >20 mg/kg. Mean zinc concentrations ranged from 18 to 250 mg/kg and were lowest in muscle for all species.

Table 11. Mean metal concentrations in sediment from Kanuti National Wildlife Refuge, 1985. Each concentration is the mean of three replicate samples expressed as mg/kg dry weight.

Site	Date	As	Cd	Cu	Fe	Pb	Mn	Hg	Ni	Zn
1	06/24	7.3	0.32	35.0	32200	8.5	680	0.06	38.0	110
2	06/25	2.7	0.10	26.0	14000	11.0	259	0.05	19.0	35
2	08/19	2.4	0.18	6.6	19300	2.7	206	<0.05	18.0	52
3	06/25	5.1	0.07	15.0	19600	4.7	438	<0.05	22.0	58
4	06/25	6.8	<0.05[a]	22.0	24800	7.3	434	0.05	31.0	68
5	06/26	4.1	0.44	17.0	19400	4.4	348	<0.05	21.0	49
7	06/26	3.1	0.40	15.0	14100	4.9	258	0.05	18.0	43
8	08/20	3.0	0.29	4.2	6540	2.0	117	<0.05	5.0	19
9	08/01	4.2	0.10	15.0	18500	5.5	315	<0.05	19.0	42

[a] The less than sign (<) indicates all analyses were <LOD. LODs were as follows: As 2.0, Cd 0.05, Cu 3.0, Fe 10, Pb 2.0, Mn 10, Hg 0.05, Ni 1.0, Zn 15.

Table 12. Mean metal concentrations in sediment from Kanuti National Wildlife Refuge, Alaska, 1987. Each concentration is the mean of three replicate samples expressed as mg/kg dry weight.

Site	Date	As	Ba	Be	Cr	Cu	Pb	Mn	Ni	Sr	Zn
1	05/25	7.53	28.3	<0.17[a]	13.3	33.7	7.47	706	27.7	89.0	89.0
2	05/26	6.10	22.7	0.16	11.5	21.3	7.63	482	21.7	50.3	63.0
3	05/26	2.93	57.7	-[b]	11.1	13.7	<5.00	399	14.7	9.8	41.0
4	05/26	5.60	23.3	-	12.7	22.3	9.03	515	24.0	65.0	70.0
5	05/27	3.27	65.3	<0.17	13.0	13.7	<5.00	317	17.0	14.0	43.3
6	05/27	4.17	88.3	0.19	16.7	15.0	4.70	341	18.3	15.9	58.7
7	05/27	3.97	79.0	-	15.7	20.3	<5.00	382	20.0	18.0	48.3
10	05/28	5.50	61.7	-	13.3	18.3	-	421	20.7	17.7	52.7
11	05/28	4.97	52.7	-	13.0	17.3	-	373	19.0	15.0	46.7
12	05/29	5.50	52.7	-	13.7	16.3	-	395	19.3	13.3	46.3
13	05/29	4.90	90.7	-	13.3	20.3	<5.00	510	18.0	13.0	47.0

[a] The less than sign (<) indicates all analyses were <LOD.

[b] The dash (-) indicates that two of the analyses were <LOD. When one of the analyses was <LOD, 0.5(LOD) was substituted for the LOD in calculation of the mean. LODs (mg/kg dry weight) were as follows: As 0.8, Ba 0.3, Be 0.17, Cd 0.5, Cu 0.5, Fe 13, Pb 5.00, Ni 2.0, Sr 1.0, Sn 50, Tl 50, V 0.3, Zn 0.2.

Table 13. Mean metal concentrations in sediment from Kanuti National Wildlife Refuge, Alaska, 1988. Each concentration is the mean of three replicate samples expressed as mg/kg dry weight.

Site	Date	As	Ba	Be	Cd	Cu	Fe	Pb	Ni	Sr	Sn	Tl	V	Zn
2	08/22	9.7	35.8	0.18	-[a]	27.6	29067	12.0	32.4	73.6	9.3	330	16.2	87
20	08/22	5.4	32.7	0.23	0.42	26.5	32333	12.8	35.5	52.9	9.7	347	15.6	92
22	08/22	13.4	41.2	0.21	0.64	36.2	31467	14.5	37.5	78.4	8.8	354	20.9	109
23	08/23	10.3	23.8	0.18	0.51	24.5	26133	10.2	30.3	96.4	10.1	290	14.9	77
24	08/23	9.9	23.8	0.17	0.46	29.5	28333	11.6	33.2	94.1	11.1	316	17.5	105
25	08/23	9.7	27.6	0.21	-	28.7	28933	11.6	31.1	137.7	11.2	331	15.6	81
26	08/23	11.3	20.6	0.19	<0.50[b]	25.9	26267	11.1	29.0	143.0	9.9	296	14.4	74

[a] The dash (-) indicated that two of the analyses were <LOD. When one of the analyses was <LOD, 0.5(LOD) was substituted for the LOD in calculation of the mean.

[b] The less than sign (<) indicates all analyses were <LOD. LODs (mg/kg-dry weight) were as follows: As 1.0, Ba 0.5, Be 0.1, Cd 0.5, Cu 0.5, Fe 10, Pb 5.0, Mo 1.0, Ni 2.0, Sn 10, Sr 1.0, Tl 10, V 1.0, Zn 1.0.

Table 14. Scheffe' groupings expressing significant differences of mean metal concentrations at seven sediment sample sites at Kanuti National Wildlife Refuge, Alaska, 1988. Sample sites containing the same letter did not differ significantly in metal concentrations. Concentrations decrease by letter designation (i.e., A is highest concentration, B is next highest, etc.).

Site	As	Ba	Cu	Fe	Pb	Ni	Sr	Tl	V	Zn
2	AB	AB	BCD	ABC	AB	BCD	D	ABC	B	BC
20	B	BC	CDE	A	AB	AB	E	AB	B	B
22	A	A	A	AB	A	A	CD	A	A	A
23	AB	D	E	C	B	CD	B	C	B	CD
24	AB	D	B	BC	AB	BC	BC	ACB	B	A
25	AB	CD	BC	BC	AB	CD	A	ABC	B	BCD
26	AB	D	DE	C	AB	D	A	BC	B	D

Table 15. Metals concentrations of kidney, liver, muscle and whole body, and total length and weight of Arctic grayling (*Thymallus arcticus*), humpback whitefish (*Coregonus pidschian*), least cisco (*Coregonus sardinella*), northern pike (*Esox lucius*), and whitefish (*Coregonus* sp.) collected from Kanuti National Wildlife Refuge, Alaska, 1985. Metal concentrations, total length, and weight are expressed as mg/kg dry weight, mm, and gm, respectively.

Site	Species[a]	FL[b]	Wt[c]	Tissue[d]	Date	Al	Cd	Cr	Fe	Hg	Mn	Ni	Pb
1	NP	460	920	K	08/22	4.6	0.51	<0.10[e]	398	NA[f]	3.2	1.01	1.01
1	NP	460	920	L	08/22	<2.0	<0.06	<0.10	405	0.23	6.3	<0.09	<0.10
1	NP	460	920	M	08/22	16.7	<0.06	0.27	56	0.63	19.2	0.27	<0.10
1	NP	389	430	W	08/22	39.4	<0.06	0.34	104	0.39	20.1	0.29	<0.10
3	LC	354	490	K	08/19	201.2	1.22	<0.10	933	NA	84.8	1.22	1.83
3	LC	354	490	L	08/19	17.4	<0.06	<0.10	253	0.63	37.7	<0.09	<0.10
3	LC	354	490	M	08/19	320.4	<0.06	1.53	706	0.34	106.0	1.19	<0.10
3	NP	365	340	W	08/19	21.0	<0.06	0.24	69	0.42	26.2	<0.09	<0.10
3	NP	365	340	W	08/19	18.2	<0.06	<0.10	94	0.29	37.1	<0.09	<0.10
5	AG	376		K	06/27	24.9	1.21	<0.10	576	NA	2.4	0.61	<0.10
5	AG	376		L	06/27	10.5	0.48	<0.10	423	0.43	5.8	<0.09	<0.10
5	AG	376		M	06/27	42.2	<0.06	0.34	149	0.38	23.3	0.25	<0.10
5	AG	370		W	06/27	83.0	<0.06	0.38	187	0.25	21.3	0.34	<0.10
5	AG	390	700	W	06/27	43.8	<0.06	0.80	196	0.25	21.6	0.40	<0.10
5	HW	447		K	06/27	3.6	2.50	<0.10	630	0.60	1.4	0.54	<0.10
5	HW	447		L	06/27	<2.0	<0.06	<0.10	167	0.15	2.5	<0.09	<0.10
5	HW	447		M	06/27	34.6	<0.06	0.35	86	0.17	16.7	0.35	<0.10
5	NP	712		K	06/27	11.1	0.45	0.35	454	4.07	2.2	0.50	<0.10
5	NP	712		L	06/27	3.9	<0.06	<0.10	473	2.22	1.6	<0.09	<0.10

Table 15, continued

Site	Species	FL	Wt	Tissue	Date	Al	Cd	Cr	Fe	Hg	Mn	Ni	Pb
5	NP	712		M	06/27	18.1	<0.06	0.41	94	3.25	12.2	0.25	<0.10
7	W	115		W	06/26	58.8	<0.06	0.94	229	0.24	12.8	0.39	<0.10
8	AG	365		K	06/27	295.0	3.45	<0.10	1027	NA	38.3	2.68	<0.10
8	AG	365		L	06/27	13.2	0.91	<0.10	422	0.59	6.3	0.45	<0.10
8	AG	365		M	06/27	32.2	<0.06	0.29	105	0.35	24.0	0.24	<0.10
8	AG	345		W	06/27	46.0	<0.06	0.38	131	0.32	23.3	0.34	<0.10
8	NP	368		K	06/27	14.0	0.52	<0.10	159	NA	3.1	<0.09	<0.10
8	NP	368		L	06/27	<2.0	<0.06	<0.10	343	NA	3.0	<0.09	<0.10
8	NP	368		M	06/27	42.9	<0.06	0.39	107	0.54	27.8	0.39	0.98

[a] AG = Arctic Grayling, HW = Humpback Whitefish, LC = Least Cisco, NP = Northern Pike, W = Whitefish;
[b] FL = Fork Length (mm); [c] Wt = Weight (gm); [d] K = Kidney, L = Liver, M = Muscle, W = Whole Body.
[e] The less than sign (<) indicates all values were <LOD.
[f] NA = No analysis.

Table 16. Metals concentrations of kidney, liver, muscle, and whole body, and total length and weight of Arctic grayling (*Thymallus arcticus*) and northern pike (*Esox lucius*) collected from Kanuti National Wildlife Refuge, Alaska, 22 July 1986. Metals concentrations, total and fork length, and weight are expressed as mg/kg dry weight, mm, and gm, respectively.

Site	Species[a]	TL[b]	FL[b]	Wt[c]	Tissue[e]	Cd	Co	Cr	Ni	Hg
14	AG	240	216	60	W	<0.20	0.77	0.98	1.17	0.26
15	NP	601	567	1250	M	<0.20	<0.50	<0.62	0.88	1.49
15	NP	601	567	1250	L	0.58	<0.50	<0.62	0.88	0.72
15	NP	601	567	1250	K	<0.20	<0.50	0.10	2.68	1.30
16	AG	386	353	360	W	<0.20	1.73	<0.62	<0.80	0.24
17	AG	557	519	1040	M	<0.20	<0.50	<0.62	<0.80	0.80
17	AG	557	519	1040	L	<0.20	<0.50	0.28	0.81	0.19
17	AG	557	519	1040	K	0.40	2.83	0.64	3.51	NA[d]
18	AG	298	272	225	W	<0.20	<0.50	<0.62	1.34	0.22
19	AG	405	363	405	M	0.27	0.75	<0.62	0.89	0.90
19	AG	405	363	405	L	0.27	<0.50	0.67	1.19	0.16

[a] AG = Arctic Grayling, NP = Northern Pike.
[b] TL = Total Length, FL = Fork Length, Wt = Weight.
[c] K = Kidney; L = Liver, M = Muscle, W = Whole Body.
[d] NA = No analysis.

Table 17. Mean metals concentrations of kidney, liver, muscle, and whole body of Arctic grayling (*Thymallus arcticus*), longnose sucker (*Catastomus catastomus*), and northern pike (*Esox lucius*) from Kanuti National Wildlife Refuge, Alaska, 1987. Metals concentrations are expressed as mg/kg-dry weight.

Site	N	Species[a]	Tissue[b]	Cd	Cr	Ni	Hg
1	2	LS	K	5.54	<0.62[c]	1.81	NA[d]
1	3	LS	L	1.29	NA[e]	0.92	0.04
1	4	LS	M	<0.20	<0.62	<0.80	0.44
1	2	NP	K	5.04	<0.62	9.13	0.29
1	2	NP	L	NA	0.99	<0.80	0.14
1	2	NP	M	<0.20	<0.62	NA	0.56
2	5	AG	W	<0.20	0.84	0.57	0.24
3	5	AG	W	NA	0.81	NA	0.25
3	3	LS	K	6.39	1.26	2.11	NA
3	3	LS	L	2.04	0.68	NA	0.22
3	3	LS	M	NA	NA	NA	0.75
3	3	NP	K	0.79	NA	1.83	1.69
3	4	NP	L	NA	<0.62	0.73	0.48
3	4	NP	M	NA	<0.62	0.85	1.74
5	5	AG	W	<0.20	0.79	1.00	0.93
6	3	LS	K	5.55	0.66	2.73	NA
6	3	LS	L	1.61	NA	1.63	0.16
6	3	LS	M	<0.20	NA	0.77	0.83
7	5	AG	W	<0.20	0.86	NA	0.37
10	5	AG	W	NA	0.94	3.81	0.19
11	3	AG	W	NA	NA	NA	0.16
12	5	AG	W	NA	0.80	1.57	0.19
13	4	AG	W	<0.20	0.80	0.91	0.15

[a] AG = Arctic Grayling, LS = Longnose Sucker, NP = Northern Pike;
[b] K = Kidney, L = Liver, M = Muscle, W = Whole Body.
[c] The less than sign (<) indicates that all values were <LOD.
[d] NA = no analysis.
[e] ≥50% of the values were <LOD. Where <50% of the values were <LOD, one-half of the LOD value was substituted for the LOD value(s), which were then used in calculation of the mean.

When kidney, liver, and muscle data from all sites were combined, numerous highly significant differences occurred among tissues within species (Table 19). Cadmium concentrations in tissue for all species were highest in kidney> liver> muscle. Mean cadmium concentrations in longnose sucker kidney were one and two orders of magnitude greater than in liver and muscle, respectively; however, a statistically significant difference was not observed.

1989 - Twenty-six fish, two marten and one mink (*Mustela vison*) were collected during 1989. QA-QC screening indicates that aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, magnesium, manganese, molybdenum, mercury, nickel, selenium, silver, strontium, thallium, and vanadium data were acceptable from 1989 samples (Table 20, Appendix K). Arsenic, beryllium, chromium, molybdenum, nickel, selenium, silver, thallium, and vanadium were not detected in any sample. Boron, cadmium, and lead were detected in three, one, and two samples, respectively. Copper, mercury, magnesium, and strontium were detected in each sample. Mercury concentrations in northern pike ranged from 0.24 to 3.20 mg/kg. The three highest values of aluminum, barium, copper, iron, manganese, and strontium were from one lake chub and two slimy sculpin whole body samples. The highest values of aluminum, barium, iron, and strontium in northern pike muscle were from the Kanuti River drainage. The highest concentrations of mercury in northern pike muscle were from fish collected at the Koyukuk (Sites 4 and 19) and South Fork Koyukuk (Site 5) rivers.

Copper concentrations in mink and marten muscle ranged from 8.30 to 13.00 mg/kg (Appendix K), higher than in any fish sample collected during 1989. Magnesium concentrations were lower, in all cases, and mercury concentrations were generally lower in mink and marten muscle than in northern pike muscle.

Metals concentrations in northern pike muscle were combined within drainages for statistical comparisons. Significantly higher concentrations of barium ($F_{2,20} = 13.4$, $P < 0.01$), iron ($F_{2,20} = 10.2$, $P < 0.01$), and strontium ($F_{2,20} = 12.7$, $P < 0.01$) were detected in fish collected from the Kanuti River drainage than in those collected from the Koyukuk and South Fork Koyukuk drainages.

Three marten hair samples were collected during late 1989. QA-QC screening indicates that antimony, barium, beryllium, cadmium, chromium, cobalt, copper, iron, magnesium, manganese, molybdenum, mercury, nickel, strontium, vanadium, and zinc data were acceptable from these samples (Appendix L). Antimony, barium, beryllium, cadmium, cobalt, molybdenum, strontium, and vanadium were not detected in any sample. Chromium was detected once at 2.4 mg/kg. Mean copper and mercury concentrations were 7.6 mg/kg and 0.39 mg/kg, respectively.

1990 - Ten sets of slimy sculpin and 14 wolf hair samples were collected during 1990. QA-QC screening indicates that aluminum, antimony, barium, beryllium, boron, cadmium, chromium, iron, lead, manganese, molybdenum, mercury, nickel, silver, strontium, thallium, tin, vanadium, and zinc data were acceptable from these samples (Table 21). Boron, silver, and thallium were not detected in any sample. Metals concentrations in slimy sculpin were combined within drainages for statistical comparisons. No significant differences occurred between sculpin collected in South Fork Koyukuk River and Middle Fork Koyukuk River drainages. The mercury concentration of wolf hair samples (Appendix M) ranged from 0.133 to 2.880 mg/kg.

Table 18. Mean metals concentrations of kidney, liver, muscle, and whole body of Arctic grayling (*Thymallus arcticus*), longnose sucker (*Catastomus catastomus*), and northern pike (*Esox lucius*) collected from Kanuti National Wildlife Refuge, Alaska, 1988. Metals concentrations are expressed as mg/kg dry weight.

Site	N	S[a]	T[b]	Date	As	B	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Se	Zn
1	2	AG	K	08/28	0.22	-	7.23	0.77	6.74	841	0.901	572	<2.00[c]	0.50	20.75	84
1	2	AG	L	08/28	0.17	0.40	3.04	0.50	13.64	263	0.670	1004	7.40	1.29	7.57	128
1	2	AG	M	08/28	0.26	0.61	<0.60	<0.60	2.03	<30	0.659	1270	<2.00	1.03	1.41	53
1	3	LS	K	08/28	0.30	-[d]	49.03	0.58	7.83	594	0.442	654	4.86	0.83	4.05	223
1	3	LS	L	08/28	0.40	1.36	4.33	0.66	42.70	1267	0.236	730	6.85	0.91	3.99	119
1	3	LS	M	08/28	0.29	0.77	<0.60	0.56	3.17	46	0.668	1343	-	0.35	1.54	42
1	5	NP	K	08/28	<0.20	-	3.48	-	10.12	366	0.259	765	4.55	-	5.20	250
1	5	NP	L	08/28	<0.20	-	<0.60	-	11.04	159	0.217	555	3.75	0.26	3.44	95
1	5	NP	M	08/28	<0.20	-	<0.60	-	-	<30	0.474	1542	2.39	0.45	1.25	17
1	2	NP	W	08/28	<0.20	0.39	<0.60	0.95	2.35	54	0.329	1310	18.53	0.24	1.42	119
20	1	LS	K	08/18	0.29	0.60	1.01	1.35	3.18	310	0.028	1140	11.10	0.46	6.02	55
20	1	LS	L	08/18	0.59	0.99	2.83	<0.60	65.20	442	0.040	775	<2.00	0.33	4.50	110
20	1	LS	M	08/18	0.34	0.25	<0.60	<0.60	1.00	15	0.207	1340	<2.00	0.31	1.38	34
22	1	AG	L	08/19	0.25	2.18	4.24	<0.60	16.10	547	1.540	698	7.25	3.00	22.70	182
22	1	AG	M	08/19	0.53	0.25	<0.60	<0.60	2.66	15	0.313	1240	<2.00	2.00	3.12	43
22	4	AG	W	08/19	0.34	-	<0.60	1.43	4.32	112	0.123	1368	22.75	1.27	3.67	111
22	1	NP	K	08/18	0.29	<0.50	1.76	0.88	7.97	473	0.131	836	3.85	0.22	4.43	232
22	2	NP	L	08/19	<0.20	<0.50	<0.60	<0.60	10.00	184	0.231	457	3.81	-	4.00	32
22	2	NP	M	08/19	0.24	0.59	<0.60	0.46	1.84	<30	0.308	1575	1.93	<0.21	1.69	18

Table 18 Cont.

Site	N	S	T	Date	As	B	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Se	Zn
23	1	AG	W	08/23	0.60	0.83	<0.60	4.93	5.08	301	0.373	975	7.47	2.23	3.19	108
23	1	LS	K	08/25	0.50	0.25	20.30	0.61	7.34	192	0.869	585	8.80	<0.21	2.34	200
23	1	LS	L	08/25	0.33	0.91	2.23	0.30	27.70	362	0.234	315	16.40	<0.21	3.02	76
23	1	LS	M	08/25	0.52	0.25	<0.60	0.85	3.39	15	0.068	1460	7.92	<0.21	2.21	30

[a] AG = Arctic Grayling, LS = Longnose Sucker, NP = Northern Pike;

[b] K = Kidney, L = Liver, M = Muscle, W = Whole Body.

[c] The less than sign (<) indicates that all values were <LOD.

[d] A dash (-) indicates that ≥ 50% of the values were <LOD. Where <50% of the values were <LOD, one-half of the LOD value was substituted for the LOD value(s), which were then used in calculation of the mean.

Table 19. Scheffe' groupings expressing highly significant differences ($P < 0.01$) of mean metal concentrations among longnose sucker (*Catastomus catastomus*) and northern pike (*Esox lucius*) kidney, liver, and muscle tissues from all sites at Kanuti National Wildlife Refuge, Alaska, 1988.

	Cd	Cu	Fe	Mg	Mn	Se	Zn
Longnose Sucker	K,L>M[a]	L>K,M		M>K,L		K,L>M	K>M
Northern Pike	K>L,M		K>L>M	M>K>L	K>M	L>M	K>L>M

[a] K = Kidney, L = Liver, M = Muscle.

Table 20. Mean metal concentrations of muscle and whole body of lake chub (*Coueseius plumbeus*), slimy sculpin (*Cottus cognatus*), northern pike (*Esox lucius*), marten (*Martes americana*), and mink (*Mustela vison*) collected from Kanuti National Wildlife Refuge, Alaska, 1989. Metals concentrations are expressed as mg/kg-dry weight.

Site	N	Species	Matrix	Date	Al	Ba	Cu	Fe	Hg	Mg	Mn	Sr
1	2	NP[a]	Muscle	07/05/89	<3[b]	0.31	0.59	5	0.52	1435	1.50	1.25
2	2	NP	Muscle	07/08/89	<3	0.10	0.40	1	0.65	1390	1.50	1.70
3	5	NP	Muscle	07/07/89	-[c]	0.27	0.34	2	1.79	1416	4.40	1.44
4	1	NP	Muscle	07/08/89	<3	0.40	0.40	<1	2.90	1330	1.00	1.70
4	1	CH	WB[d]	07/08/89	425	6.50	5.60	446	0.31	1560	27.00	54.70
5	2	NP	Muscle	07/06/89	<3	0.42	0.50	11	2.30	1380	3.85	1.35
6	2	NP	Muscle	07/06/89	3	0.48	0.65	5	1.23	1385	2.90	1.85
15	3	NP	Muscle	07/14/89	13	1.00	0.40	14	1.06	1407	3.60	3.80
17	1	NP	Muscle	07/14/89	17	0.43	0.40	21	0.34	1390	2.00	2.00
19	1	SS	WB	07/14/89	150	8.40	2.90	232	2.00	1530	68.00	58.50
20	1	SS	WB	07/05/89	750	13.00	4.40	896	0.14	1810	75.0	67.40
22	1	NP	Muscle	07/05/89	<3	<0.20	0.30	<1	0.79	1370	<1.00	0.96
43	4	NP	Muscle	07/14/89	10	0.86	0.45	11	0.78	1393	4.58	4.48
44	1	Mi	Muscle	1989	<3	0.40	8.30	274	0.23	666	1.0	0.4
44	2	Ma	Muscle	1989	6	0.25	11.50	218	0.20	875	1.00	0.3

[a] CH = Lake Chub, LS = Longnose Sucker, NP = Northern Pike, SS = Slimy Sculpin, Ma = Marten, Mi = Mink.

[b] The less than sign (<) indicates that all values were <LOD.

[c] A dash (-) indicates that ≥50% of the values were <LOD. Where <50% of the values were <LOD, one-half of the LOD value was substituted for the LOD value(s), which were then used in calculation of the mean.

[d] WB = Whole Body.

Table 21. Metal concentrations of whole body slimy sculpin (*Cottus cognatus*) composite samples collected 13 June 1990, from areas upstream of Kanuti National Wildlife Refuge, Alaska. Metal concentrations are expressed as mg/kg-dry weight.

Site	Sample Size[a]	Al	Ba	Cd	Cr	Fe	Hg	Pb	Mn	Sn	Sr	Zn
9	25	1712	20.8	0.62	17.17	4177	0.181	2.74	126.6	35.8	53.1	161
29	14	174	21.7	0.62	4.03	507	0.237	0.85	37.9	11.1	135.1	174
30	7	90	13.0	0.44	3.24	259	0.227	1.69	22.9	19.3	88.4	140
33	22	254	26.0	0.61	4.04	568	0.197	1.22	76.1	9.8	103.8	180
35	23	81	20.0	<0.35	5.02	251	0.188	2.11	20.1	14.0	121.5	182
39	1	33	21.1	<0.35	10.81	183	0.483	6.36	15.4	20.7	55.5	108
40	25	532	6.1	0.41	4.86	1455	0.266	1.31	67.1	11.7	73.4	158
45	18	253	11.7	0.41	5.58	940	0.470	1.84	34.3	11.6	70.5	165
46	2	NA[b]	NA	NA	NA	NA	0.293	0.90	NA	NA	NA	NA
47	12	421	5.3	0.81	5.79	1733	0.158	8.14	56.1	18.0	88.7	209

[a] Number of sculpin in sample.
[b] NA indicates that no analysis was performed.

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. During this study the South Fork Koyukuk River was a clear, soft water, calcium and magnesium bicarbonate-dominated stream with near neutral pH. Samples from South Fork tributary streams (Fish, Prospect and Bonanza creeks, and the Jim River) had even lower hardness and alkalinity than those from the main stem. Between 1970 and 1974, conductivity and suspended solids values in the Jim River were generally close to those measured during this study. Conductivity values in the Jim River during the early 1970's were up to 100 µS/cm (Childers et al. 1977), compared to 40 µS/cm in this study. Turbidity and suspended solids, from this study, were lower in South Fork Koyukuk River samples than in Koyukuk or Middle Fork Koyukuk river samples. Similar to the South Fork Koyukuk River, the Kanuti and Kanuti-Kilolitna rivers had soft, low alkalinity, clear water.

Koyukuk River samples had moderate hardness. Unlike South Fork Koyukuk River samples, the concentration of hardness cations in Koyukuk River samples was almost twice the concentration of alkalinity anions. Although the Koyukuk River was bicarbonate-dominated, sulfates, and to a lesser extent chlorides, likely constituted a significant portion of the anions. Sulfates are typically the second largest anion component in streams in this area of Alaska (D. Snyder, U.S. Geological Survey, pers. comm.). The pH of Koyukuk River samples was slightly alkaline, unlike those of South Fork Koyukuk River samples. Samples from Koyukuk River tributary streams, the John and Wild rivers, had similar water quality characteristics as the main stem. On 22 August 1988, samples from the Koyukuk River south of Bettles, and the John and Wild rivers near their mouths had significantly lower pH than at Sites 23, 24, 25, and 26 on the Middle Fork Koyukuk River. However, conductivity, hardness, and alkalinity did not follow the same pattern. Koyukuk River samples had higher turbidity, suspended solids, and settleable solids than the Middle Fork Koyukuk and South Fork Koyukuk river samples.

Values of pH, conductivity, hardness, and alkalinity were generally higher in samples from the Middle Fork Koyukuk River than in samples from the South Fork Koyukuk or Koyukuk rivers. Between 1970 and 1975, hardness in the Middle Fork Koyukuk River at Wiseman (near Site 24) ranged from 170 to 300 mg/L ($\bar{x}$ = 231 mg/L, n = 11). Between 1970 and 1977, alkalinity values for these sites ranged from 75 to 246 mg/L ($\bar{x}$ = 155 mg/L, n = 17) (R. Kenmitz, U.S. Geological Survey, unpubl. data). These ranges of hardness and alkalinity values encompass those measured in samples from the Middle Fork Koyukuk River from this study; however, the mean values from this study are lower. Between November 1969 and September 1974, conductivity was measured between approximately 180 µS/cm to 500 µS/cm (Childers et al. 1977) on the Middle Fork Koyukuk River at Wiseman. These values are lower than those of samples collected at Sites 24, 25, 26, and 40 from this study. Values of pH, conductivity, and alkalinity of samples from the Middle Fork Koyukuk River at Coldfoot (Site 23) are in general agreement with those measured by Nauman and Kernodle (1973) during June 1971. They noted that conductivity ranged from 200 to 240 µS/cm within a 24-hr. period. As with the Koyukuk River samples, those from the Middle Fork Koyukuk River had a high hardness/alkalinity ratio.

With few exceptions, high turbidity and suspended solids measurements occurred during the 24-25 June 1985 and 25-26 May 1987 sample periods. All measurable settleable solids measurements occurred during these periods. These high measurements are probably a result of rainfall. Bettles received 1.8 cm, 2.2 cm, and 3.2 cm of rainfall (National Weather Service, unpublished data), respectively, during the three 1-week periods preceding these sample dates. June 24, 1985, was preceded by 2 days of increasing stream discharge (USGS 1985), and 25 May 1987, had the highest discharge of the year to that date on the Middle Fork Koyukuk River at Wiseman (USGS 1987). Suspended solids and turbidity values were highest on the Koyukuk River followed by the Middle Fork Koyukuk River and the South Fork Koyukuk River. Settleable solids were measurable in five instances and four of those instances were from the Koyukuk River. However, the Middle Fork Koyukuk River was not sampled during either of the two high-water periods mentioned.

Trace Elements in Water

Surface waters in and upstream of the Kanuti Refuge were relatively uncontaminated by metals. Arsenic, cadmium, chromium, mercury, and thallium were either not detected or detected at low concentrations. Dissolved copper levels in uncontaminated freshwaters usually range from 0.5 to 1.0 µg/L, increasing to ≥2 µg/L in urban areas (Moore and Ramamoorthy 1984). Total recoverable copper concentrations from 1985 and 1987 ranged from 2 µg/L and 8 µg/L which is well below the EPA Water Quality Criteria (WQC) (EPA 1986) for copper of 12 µg/L (at hardness = 100 mg/L). Total recoverable copper concentrations from this study are similar to those reported for an unmined stream (LaPerriere et al. 1985). LaPerriere et al. (1985) reported that total recoverable copper ranged from 37 to 170 µg/L from a mined watershed. Total copper was up to 31 µg/L in samples from Site 2 in 1985 but did not exceed 14 µg/L in samples taken in subsequent years. The two highest values for total copper, 31 µg/L and 20 µg/L, coincided with the two highest turbidity values reported during this study. The greater Koyukuk River drainage contains highly mineralized areas, including numerous copper deposits (Cobb 1972a, b, c), and total copper concentrations within the range reported may be the result of the natural weathering of rock. Extensive placer mining has occurred and continues to occur in the greater Koyukuk River drainage, and this, too, could result in increased copper concentrations. LaPerriere et al. (1985) also reported that concentrations of total arsenic, lead, copper, and zinc were significantly higher in streams below active mining sites. Concentrations of these metals from samples taken above (Site 11) and below (Site 10) inactive placer mines at Gold Bench, South Fork Koyukuk River, were almost identical during 1987 indicating that no contamination of the river was occurring from this site at that time.

Total iron concentrations ranged from 0.39 mg/L (Site 22, Wild River) to 30.00 mg/L (Site 2, Koyukuk River). Total iron concentrations in samples generally increased going downstream except in the Middle Fork Koyukuk River. LaPerriere et al. (1983) reported that iron concentrations were much higher in mined streams than in unmined streams; however, iron enrichment due to placer mining was apparently not occurring in the Middle Fork Koyukuk River, the most intensely mined section of the river, because total iron concentrations decreased among sample sites progressing downstream in this section of the river. Iron concentrations exceeded the chronic WQC (EPA 1986) of 1.00 mg/L in many refuge waters as well as in samples upstream from the refuge. EPA recommends applying the criteria using the total recoverable method for iron. The chronic WQC for iron was exceeded in samples taken at Site 3 during 1985, in those from Sites 1-7 and 10 during 1987, and in samples collected at Sites 2, 20, and 22-26 during 1988. The Canadian guideline for the protection of freshwater aquatic life is 0.3 mg/L total iron (Canadian Water Quality Guidelines 1987), and this was exceeded at all sites sampled. Concentrations of iron in surface waters of western Canada ranged from <0.02-14.0 mg/L. The total iron concentrations found during this study are much greater than those at the Selawik National Wildlife Refuge (Mueller et al. 1992), west of the Kanuti Refuge, and are generally greater than those at the Koyukuk and Nowitna refuges (Snyder-Conn et al. 1992a, b) although the latter two refuges also generally had high iron concentrations.

High iron concentrations can impair wildlife health and reproduction. A total iron concentration of <3.0 mg/L is safe for growth and reproduction of *Gammarus minus* (Sykora et al. 1972); however, Goettl and Davies (1977) observed 100% mortality by rainbow trout (*Oncorhynchus mykiss*) eggs when exposed to 3.4 mg/L and 2.2 mg/L iron within three and six weeks, respectively. Death appeared to be caused by flocculated iron compounds smothering the eggs and sac-fry. No adverse effects were observed when rainbow trout fry were exposed to 3.4 mg/L iron for five months (Goettl and Davies 1977). Iron hydroxide precipitate interferes with respiration through the chorion in fish eggs, and impairs gill function by occlusion of the lamellae (Sykora et al. 1972). Total iron concentrations are likely the relevant values, over total recoverable, if smothering is the mode of death and biologic uptake is not involved. We found that concentrations of total iron frequently exceed those that cause mortality in rainbow trout eggs (Goettl and Davies 1977).

Total recoverable manganese was detected in concentrations greater than the WQC (EPA 1986) for domestic water supplies (50 µg/L) from samples taken at Sites 1, 2 and 4 (Koyukuk River), and 3, 5 and 7 (South Fork Koyukuk River) in 1987. The criterion was set at 50 µg/L to prevent unwanted color and taste in public drinking water supplies. Manganese is not toxic in concentrations found during this study.

In general, total, total recoverable and dissolved lead, and total recoverable iron and manganese concentrations (the only data sets in common for 1985 and 1987) were several times greater in 1987 than in 1985. Although both sets of analysis passed the QA/QC criteria, laboratory or sample collection error may be the cause of these differences.

The results of comparisons of metals concentrations in samples from the Kanuti refuge with those from the Koyukuk, Nowitna, and northern Innoko refuges are mixed. Total lead concentrations from 1987 are less than, and total and dissolved lead concentrations from 1985 were similar to, those from Koyukuk and northern Innoko National Wildlife refuges (Snyder-Conn et al. 1992a), southwest of the Kanuti Refuge. Total and dissolved nickel and zinc concentrations were in the same range as those from the Koyukuk, Nowitna, and Northern Innoko refuges (Snyder-Conn et al. 1992a, b). Total manganese concentrations were greater than those in the Koyukuk, Nowitna and northern Innoko refuges, and dissolved manganese concentrations were in the same range as those from these refuges (Snyder-Conn et al. 1992a, b).

In general, samples from Sites 1, 2, and 4 (Koyukuk River) had the highest total arsenic, copper, iron, lead, manganese, nickel, and zinc concentrations of any sites. Many of the differences in metals concentrations between the Koyukuk River and South Fork Koyukuk River drainage were statistically significant. Moore and Ramamoorthy (1984) reported that particulates contain 12-97% of the copper, 47-72% of the lead, 97-98% of the nickel (Yukon River data), and 10-78% of the zinc transported by rivers. In our study, concentrations of total copper, iron, manganese, nickel, and zinc were highly correlated with turbidity for 1985, and concentrations of total aluminum, iron, and manganese were highly correlated with turbidity and suspended solids for 1988. The Koyukuk River likely has higher concentrations of these metals because particulates are more highly mobilized in this river than in other rivers sampled for this study, as evidenced by higher suspended solids and turbidity levels.

Trace Elements in Sediments

There was good general agreement in metals concentrations in sediments between years. The concentrations of arsenic, cadmium, copper, lead, and nickel that we found are generally within the upper portion of ranges listed as uncontaminated sediments (Moore and Ramamoorthy 1984, Bennett and Cubbage 1991). Mercury was rarely detected, and only at the LOD. Although concentrations of zinc in samples taken at several sites were greater than those listed for uncontaminated sediments by Moore and Ramamoorthy (1984; <50 mg/kg), concentrations were far below those of sites listed as contaminated by industrial pollution. These streams drain areas with highly mineralized parent rock and elevated metals concentrations in sediment are a likely result. The U.S. Geological Survey (Cobb 1972a, b, c) has identified many metal deposits in the greater Koyukuk River drainage. The Squirrel River, near the Selawik refuge, also drains highly mineralized areas. Karl et al. (1985) performed semi-quantitative analyses of headwater sediments in the Squirrel River drainage (Omar River) and reported concentrations of barium ($\bar{x}$ = 1,100 mg/kg), copper ($\bar{x}$ = 54 mg/kg), and zinc ($\bar{x}$ = 333 mg/kg). They considered these values to be greater than twice normal background concentrations. Even so, these values are far more than twice the values found in the Kanuti Refuge area.

As with total metals in water, sediment samples from the Koyukuk River (Sites 1, 2, and 4) generally had higher concentrations of metals than sediment samples from the South Fork Koyukuk River drainage (Sites 3 and 5 to 13). Statistically significant differences occurred between sediments of these two river systems for copper, manganese, nickel, and zinc. However, barium concentrations in samples from the Jim River (Site 13) were significantly greater than those from the Koyukuk River (Site 4). In general, samples from South Fork Koyukuk River sediments (Sites 3, 5 to 7, and 10 to 13) had the highest barium concentrations. For 1988, samples from the Wild River (Site 22) had the highest values of arsenic, barium, cadmium, copper, lead, nickel, thallium, vanadium, and zinc, and the second highest value of iron.

During 1987, sediment samples were collected below and above the Gold Bench placer gold mine. Mean concentrations of arsenic, barium, manganese, nickel, strontium, and zinc in these samples were 10-15% higher at the downstream site; however, these differences are not significant because the standard deviations of these analyses were 5-10%. Except for barium, these concentrations are less than those of Koyukuk River sites.

Concentrations of arsenic in samples from the Kanuti refuge were greater than, and zinc concentrations were similar to, those from the Koyukuk and northern Innoko (Snyder-Conn et al. 1992a), Nowitna (Snyder-Conn et al. 1992b), and Selawik refuges (Mueller et al. 1993). Copper concentrations in samples from the Kanuti refuge were slightly greater, and barium concentrations were far less, than those from Selawik National Wildlife Refuge (Mueller et al. 1993). Sediment mercury concentrations in the two refuges were similar. Chromium concentrations from Nowitna refuge (Snyder-Conn et al. 1992b) were less than those from the Kanuti refuge.

Trace Elements in Fish

Arctic grayling, northern pike, and least cisco are highly migratory species (Morrow 1980) and, thus, assigning the origin of contaminants found in these species is difficult, if not impossible. Radio-tagged Arctic grayling have migrated 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). Least cisco undergo extensive pre- and postspawning migrations. Longnose suckers apparently do not undertake any definite migrations, but wander more or less randomly in streams. By fall, longnose suckers abandon the upper reaches of streams. Slimy sculpins have rather sedentary habits and do not migrate, therefore, can be more indicative of local conditions than other fish species.

Inter-Specific Differences in Trace Element Accumulations

Longnose sucker, least cisco, and slimy sculpin differed in patterns of metal accumulation. Longnose sucker had higher concentrations of cadmium and copper than other species collected during the same time period. Least cisco from 1985 had either the highest or second highest values of aluminum, chromium, manganese, nickel, and lead. For 1989, least cisco and slimy sculpin whole bodies had much higher concentrations of aluminum, barium, copper, iron, manganese, and strontium than did northern pike muscle. During 1990, slimy sculpin were collected from streams along the Dalton Highway in the South Fork and Middle Fork Koyukuk rivers and their tributaries. Aluminum concentrations in these fish were comparable to other slimy sculpin and least cisco from this study. Slimy sculpin from 1990 generally had higher values of aluminum, barium, chromium, and manganese than all other species, regardless of tissue type. Northern pike consistently had the highest mercury concentrations of all species, regardless of tissue type.

Tissue Differences in Metal Accumulation

Cadmium, copper, magnesium, mercury, nickel, selenium, and zinc accumulated differentially in tissues, regardless of species. Cadmium accumulates primarily in major organ tissues rather than muscle (Moore and Ramamoorthy 1984). Cadmium concentrations, in each fish, were kidney> liver> muscle, in 1988. This was also generally the pattern of cadmium concentrations for fish in other years. For longnose sucker and northern pike, cadmium and magnesium concentrations in kidney were significantly greater than in liver (magnesium only for northern pike) and muscle. For each species, the rank of mean copper concentrations was liver> kidney> muscle. Jenkins (1980) reported the rank of copper concentrations for northern pike in Ontario as liver> kidney> gill, and Miller et al. (1992) reported the rank of copper in white sucker (*Catostomus commersoni*) as liver> kidney> ovary> gill> muscle. Nickel concentrations in longnose sucker kidney in 1987 were significantly greater than in muscle.

No consistent pattern of mercury accumulation was observed among tissues. Mercury concentrations were greatest in kidney in 1985, but they were greatest in muscle in 1986, 1987, and 1988. In 1987, mercury concentrations were significantly greater in muscle than in liver of longnose sucker and northern pike. As in this study, mercury concentrations at the Nowitna (Snyder-Conn et al. 1992b) and Selawik (Mueller et al. 1993) refuges were greater in muscle than in liver or kidney.

In 1988, zinc concentrations in kidney were significantly greater than in liver (longnose sucker) and muscle (longnose sucker and northern pike). Miller et al. (1992) reported the rank of zinc in white sucker as liver> kidney> ovary/bone/testis> gill> muscle.

Cobalt appeared to concentrate in kidney, liver, and muscle tissue in a nondifferential manner. As an essential nutrient, cobalt concentrations may be homeostatically controlled.

Except for magnesium, metals data from the ICPP analyses for 1989 are generally lower than corresponding values for other years. The reason for these differences is unknown.

Trace Element Comparisons

The U.S. Fish and Wildlife Service's National Contaminant Biomonitoring Program (NCBP) is designed to monitor contaminant concentrations in biota throughout the United States. From late 1984 to early 1985, 315 composite samples of whole fish were collected from 109 sites throughout the United States as part of the NCBP (Schmitt and Brumbaugh 1990). These samples were analyzed for metals and metalloids. The data were expressed in wet weight; however, they have been transformed to dry weight, assuming 75% moisture, for comparative purposes.

Arsenic

All mean arsenic concentrations from 1988 were well below the range of 85th percentile concentrations from NCBP (0.88 to 1.52 mg/kg) (Schmitt and Brumbaugh 1990). Arsenic concentrations in longnose sucker tissue and northern pike muscle were within the range reported for whole longnose sucker in New York and northern pike muscle in New York and Wisconsin (Jenkins 1980). In addition, all arsenic concentrations were within the range reported from the Upper Mississippi River for common carp (*Cyprinus carpio*) and bluegill (*Lepomis macrochirus*) (Wiener et al. 1981). Arsenic concentrations do not appear to be elevated in the Kanuti refuge.

Cadmium

Whole body cadmium concentrations of all species except slimy sculpin were far below the NCBP 85th percentile concentration range (Schmitt and Brumbaugh 1990). Four of 10 slimy sculpin composite samples collected during 1990 had cadmium concentrations greater than the NCBP 85th percentile. The highest cadmium concentration in slimy sculpin, 0.81 mg/kg, approached the NCBP maximum reported concentration of 0.88 mg/kg.

The mean cadmium concentrations in kidneys of longnose sucker, Arctic grayling, and northern pike were 16.6 mg/kg, 3.9 mg/kg, and 2.2 mg/kg, respectively. Similarly, cadmium concentrations in the Koyukuk and Nowitna refuges were higher in longnose sucker than in northern pike and Arctic grayling (Snyder-Conn et al. 1992a, b).

Cadmium was either not detected or in comparatively low concentrations in muscle. All concentrations of cadmium in muscle were less than those reported by Bohn and Fallis (1978) in Arctic char muscle (up to 2.3 mg/kg), from an unpolluted high Arctic lake. The ranges of cadmium in whole common carp and bluegill in the Upper Mississippi River were 0.05 to 0.29 mg/kg and 0.009 to 0.106 mg/kg, respectively (Wiener et al. 1981). Two whole Arctic grayling and seven of nine slimy sculpin composite samples from the our study exceeded these ranges. Other fish may have exceeded these concentrations but high LODs, especially in 1988 and 1990, precluded this determination. The mean value of cadmium in whole longnose sucker from the NCBP survey in 1984 was 0.28 mg/kg (Schmitt and Brumbaugh 1990). The mean cadmium concentration in Arctic grayling from the Chena River near Fairbanks in 1984 was 0.04 mg/kg (Schmitt and Brumbaugh 1990). Cadmium concentrations in liver of northern pike, and muscle in northern pike and Arctic grayling from this study were similar to those reported for the Nowitna refuge (Snyder-Conn et al. 1992b). The mean cadmium concentration in longnose sucker kidney from the Nowitna refuge was 5.6 mg/kg (n = 2) (Snyder-Conn et al. 1992b), similar to results from this study for 1987. Cadmium concentrations in longnose sucker kidney from this study were much greater in 1988.

Cobalt

Whole body Arctic grayling had higher concentrations of cobalt ($\bar{x}$ = 1.06 mg/kg) than in kidney, liver, and muscle of longnose sucker and northern pike. Cobalt was detected only once for 1988, at 3.55 mg/kg in a longnose sucker kidney; however, the analysis for that set of samples had a very high LOD of 3.0 mg/kg. In northern pike from 1986 and 1987 (possibly low values), cobalt was detected in one of six kidneys (0.52 mg/kg) and one of seven livers (0.59 mg/kg), but was not detected in muscle. Cobalt was not detected in northern pike kidney at the Nowitna refuge (n = 9) (Snyder-Conn et al. 1992), but the LOD of 0.9 mg/kg was high; however, cobalt was detected (1.4 mg/kg) in one of two sheefish kidneys. Wren and McCrimmon (1983) reported mean concentrations of 1.48 mg/kg (assuming 75% moisture) for rainbow smelt (*Osmerus mordax*) and lake trout (*Salvelinus namaycush)* muscle (ranges were 1.20 to 1.56 mg/kg and 1.12 to 2.28 mg/kg, respectively) from a Precambrian shield lake in Canada.

Copper

Copper concentrations in whole Arctic grayling, least cisco, and slimy sculpin were as great as or greater than the NCBP 85th percentile (Schmitt and Brumbaugh 1990). Miller (1983) reported that copper concentrations in whole fish from the Ohio River and selected tributaries ranged from 0.37 to 1.9 mg/kg, also less than whole fish from our study. Copper concentrations in Arctic grayling muscle from this study were similar to those from the Koyukuk Refuge (Snyder-Conn et al. 1992a); concentrations in northern pike muscle were slightly less than those from the Koyukuk Refuge.

Mercury

Mercury concentrations were generally within the range reported for uncontaminated or slightly contaminated areas (Jenkins 1980; Lowe et al. 1985). 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 in the contiguous 48 states. Many of these sites were suspected to be contaminated. The mean mercury concentration of background sites was approximately 0.36 mg/kg dry weight (assuming 75% moisture) (EPA 1992). Similarly, the geometric mean mercury concentration of NCBP whole fish was 0.4 mg/kg dry weight (assuming 75% moisture) (Schmitt and Brumbaugh 1990). From the present study, mercury was detected in each fish regardless of location. Mercury concentrations in whole body, muscle, kidney, and liver samples ranged from 0.04 mg/kg in a longnose sucker liver to 4.07 mg/kg in a northern pike kidney. Five of 34 whole fish (<~400 mm in length) had mercury concentrations greater than 0.4 mg/kg. Only one whole body analysis for mercury, a slimy sculpin composite from Site 19 (Henshaw Creek), exceeded the NCBP 85th percentile of 0.68 mg/kg (Schmitt and Brumbaugh 1990). All other slimy sculpin had less than 0.5 mg/kg mercury. A small bias exists in comparisons of whole fish data from this study with EPA (1992) and Schmitt and Brumbaugh (1990). Analysis of whole fish from this study were performed on fish <~400 mm in length, but both EPA (1992) and Schmitt and Brumbaugh (1990) analyzed adult fish which are more likely to have higher mercury concentrations. The mean mercury concentration of muscle from all suckers in EPA (1992) studies was 0.14 mg/kg (n = 9). Mean mercury concentrations in longnose suckers from this study were higher at 0.31 mg/kg (n = 3) (1988) and 0.65 mg/kg (n = 10) (1987).

Northern pike had the highest mercury concentrations in this study with mean concentrations in muscle ranging up to 3.25 mg/kg in northern pike. Many factors affect inter- and intraspecies-specific variation in accumulation and retention of mercury in fish (Sorensen 1991). In this instance, diet may certainly be a factor. Northern pike are the only strict piscivores collected during this study. Arctic grayling tend to be more insectivorous, longnose suckers feed off of the bottom (e.g., plant material, insects, mollusks, crustaceans), slimy sculpin are insectivorous, and least cisco feed primarily on zooplankton and immature insects (Morrow 1980). We found mercury concentrations in liver and kidney of northern pike similar to those from the Selawik refuge (Mueller et al. 1993), but mercury in northern pike muscle was lower than at the Nowitna (Snyder-Conn et al. 1992b) and Selawik (Mueller et al. 1993) refuges. Mercury concentrations in Arctic grayling from the Kanuti and Selawik refuges (Mueller et al. 1993) also were similar. No significant correlations occurred between mercury concentrations in northern pike muscle or kidney, and length or weight. Mercury concentrations in whole Arctic grayling also were not significantly correlated with length or weight. Similar results were obtained for the Selawik Refuge (Mueller et al. 1993), indicating that the varying migration patterns of northern pike and Arctic grayling likely interfere with identification of mercury source areas.

Nickel

High values of nickel were observed in Arctic grayling, least cisco, and northern pike. Nickel was detected in 29 of 40 liver, kidney, muscle, and whole body samples of fish in concentrations between <0.8 and 16.60 mg/kg. The highest concentrations in longnose sucker, northern pike, and Arctic grayling were in kidney; however, occurrence was sporadic. The highest nickel concentrations were at Sites 1, 2 (Koyukuk River), and 23 (Middle Fork Koyukuk River). The source of the nickel is unknown; however, Cobb (1974) notes two occurrences of nickel within the Kanuti refuge, both in the Kanuti River drainage.

Nickel was also detected sporadically in the Koyukuk, Nowitna, and Selawik refuges (Snyder-Conn et al. 1992a, b; Mueller et al. 1992). Maximum nickel concentrations were 17.70 mg/kg in northern pike muscle from the Koyukuk refuge (Snyder-Conn et al. 1992a) and, 1.09 mg/kg and 2.72 mg/kg in Arctic grayling and northern pike muscle, respectively, from the Nowitna Refuge (Snyder-Conn et al. 1992b). Northern pike from the Selawik Refuge had nickel up to 25.7 mg/kg of nickel (Mueller et al. 1992). High nickel concentrations may be widespread in interior and northwestern Alaska.

Nickel does not biomagnify. Nickel concentrations seldom exceed 4 mg/kg in fish from industrialized areas (Moore and Ramamoorthy 1984) and only one sample from this study, a northern pike kidney, exceeded 4 mg/kg. Jenkins (1980) reported nickel values in northern pike from <0.8 to 15.2 mg/kg (assuming 75% moisture). In the Illinois River, mean concentrations in omnivorous and carnivorous fish were 0.72 mg/kg and 0.52 mg/kg, respectively (Moore and Ramamoorthy 1984). The highest nickel concentration recorded in a survey of Pennsylvania fish from 14 sites was 0.41 mg/kg (Rampala 1984). Wren and MacCrimmon (1983) found up to 8.4 mg/kg nickel in lake trout from a Canadian precambrian shield lake. Although nickel is a required nutrient at low concentrations in many species, little information is available on the effects of nickel body burdens on fish and wildlife.

Lead

Lead occurred sporadically in concentrations as high as 8.14 mg/kg and in samples from all species; however, lead was detected most consistently and at the highest concentrations in slimy sculpin. The NCBP 85th percentile concentration of lead in whole body analyses was 0.88 mg/kg (Schmitt and Brumbaugh 1990). Excluding slimy sculpin, 2 of 10 whole body analyses, both Arctic grayling, had lead concentrations greater than the NCBP 85th percentile concentration. Nine of 10 slimy sculpin composite samples from 1990 exceeded the NCBP 85th percentile concentration; however, the gut contents of sculpin were not removed prior to analysis and sediment in the gut could have affected the results. Lead was detected in only 1 of 25 muscle samples from the Koyukuk refuge (Snyder-Conn 1993a). In our study, lead occurred in 6 of 14 muscle samples and whole fish from 9 of 13 sites had >1.0 mg/kg lead.

Little biomagnification of lead occurs in the food chain, and there is generally no correlation between residues and feeding habits (Moore and Ramamoorthy 1984). In the Illinois River, mean concentrations in omnivorous and carnivorous fish were 0.65 mg/kg and 0.62 mg/kg, respectively (Moore and Ramamoorthy 1984). The Ohio River and tributaries had 0.1 to 2.6 mg/kg lead in whole fish (Miller 1983).

Zinc

Zinc concentrations were highest in kidney and as great as 250 mg/kg. Eight of nine slimy sculpin from 1990 exceeded the NCBP 85th percentile concentration for whole body analyses of 137 mg/kg (Schmitt and Brumbaugh 1990); whole body analysis of other fish species did not exceed this concentration. The mean concentration of zinc in northern pike muscle from 1988 in our study was 17 mg/kg (n=7); zinc concentrations ranged from 15.1 to 21.8 mg/kg. Zinc concentrations from the Koyukuk Refuge were very similar: the mean zinc concentration in northern pike muscle was 17.5 mg/kg and the range was from 14.5 to 25.9 mg/kg (Snyder-Conn et al. 1993a). Zinc concentrations at the Nowitna Refuge were higher and ranged from 74 mg/kg to 131 mg/kg (Snyder-Conn et al. 1993b). Mean muscle burdens of zinc in yellow perch (*Perca flavescens*), bluegill, and black crappie (*Pomoxis nigromaculatus*) from industrial and recreational zone rivers in the United States ranged from 101 to 109 mg/kg (Moore and Ramamoorthy 1984).

CONCLUSIONS

No effects of off-refuge placer mining within the refuge were found. However, this study was not designed to specifically examine the effects of placer mining on the refuge, but to provide baseline data in the event of mining near the refuge boundaries.

Water quality characteristics of rivers sampled during this study are typical of uncontaminated rivers which are calcium- and magnesium-bicarbonate based. Except for iron and manganese, surface waters did not exceed state water quality standards and contained low concentrations of metals and other trace elements. Iron concentrations in water were elevated in all major and most minor drainages sampled during this study. Koyukuk River samples generally had the highest concentrations of arsenic, copper, iron, lead, manganese, nickel, and zinc of the three major drainages addressed.

Metals concentrations in sediment were generally indicative of uncontaminated sediments. The Koyukuk River generally had the highest concentrations of arsenic, copper, lead, nickel, and zinc in sediment of the three major drainages addressed. The Wild River had the highest values of arsenic, barium, cadmium, copper, lead, nickel, thallium, vanadium, and zinc, and the second highest value of iron in sediment.

Longnose sucker, least cisco, and slimy sculpin showed different patterns of metals accumulation. Least cisco accumulated aluminum, copper, iron, lead, manganese and nickel and, longnose sucker accumulated cadmium and copper. Slimy sculpin accumulated aluminum, barium, cadmium, copper, iron, lead, manganese, strontium, and zinc more than other species. Northern pike had the highest mercury concentrations.

Concentrations of arsenic, cadmium, and zinc were not elevated in fish tissue on the Kanuti Refuge. Copper concentrations in whole Arctic grayling, least cisco and slimy sculpin, and cadmium concentrations in 4 of 10 slimy sculpin from 1990 were as great as or greater than the NCBP 85th percentile for whole fish. Lead was detected in high concentrations in slimy sculpin composite samples. Concentrations of mercury in fish tissue were within the range reported for uncontaminated conditions. Sporadic high concentrations of nickel in fish tissue occurred within the refuge.

RECOMMENDATIONS

These recommendations are intended to assist investigators in planning studies designed to fill data gaps in the Kanuti Refuge baseline database. A complete baseline database will allow comparisons for determining impacts from development within and adjacent to the Kanuti Refuge.

1. Baseline data (water quality and metals) metals for the following rivers upstream and within the Kanuti NWR are inadequate or missing: the North Fork of the Koyukuk River, Middle Fork of the Koyukuk River, Wild River, John River, Henshaw Creek, Kanuti River, Kanuti-Kilolitna River, and Kanuti-Chalatna Creek. Resampling of the Koyukuk and Wild rivers are particularly important because these rivers have the greatest potential for contaminant or water quality impacts within the refuge.

2. Additional water quality data are desirable for all major rivers in and upstream from Kanuti NWR. The data in this study do not adequately characterize the range of water quality conditions that may occur in any river system.

3. Precise, accurate data for Kanuti NWR river waters are lacking for arsenic, cadmium, chromium, copper, mercury, nickel, and zinc. In this study, data on these trace elements failed QA-QC criteria or did not meet holding time requirements (mercury).

4. Precise, accurate data for Kanuti NWR river sediments are also needed for mercury and chromium due to inadequate data quality in this study. Total digestions, rather than incomplete digestions, for metals should be requested on sediments to improve recovery rates of metals.

5. Inadequate or no data for metals concentrations in fish were obtained in the Koyukuk, Middle Fork Koyukuk, John, Wild Kanuti, Kanuti-Kilolitna rivers, and Henshaw and Kanuti-Chalatna creeks. Additional data should be collected for these waterbodies. Metal concentrations in slimy sculpin were high from the Middle Fork Koyukuk and they should be resampled to verify these concentrations. Except at Site 23, larger fish i.e., northern pike, Arctic grayling, and longnose sucker, were not sampled. Large specimens from these species should be sampled where possible to obtain concentrations of metals in specific tissues. Based on findings in this study, priority analytes should include copper, lead, nickel, and mercury.

6. Target fish species in future studies should include slimy sculpin, longnose sucker, and northern pike. Arctic grayling proved a less desirable species for sampling, but should remain an alternate species when other species are unavailable (e.g., headwaters).

7. Future studies should include additional measures of fish health, determine migratory patterns, and assess food habits of sampled species. The significance of sediment in gut contents should also be evaluated.

8. Additional field QA samples should be included in future studies including field duplicates, blanks, and spikes and/or standards.

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

SAMPLE CATALOG

A sample catalog was prepared for each year's samples. The catalog contained study objectives; background information (including number of water, sediment, and tissue samples); previous findings and concerns; possible interfering elements in the analyses; methods of preservation and storage; instructions to the laboratory, including a description of the analyses requested together with the suggested analytical method; a list of data recipients; a cost estimate for the requested analyses; and a tabulated summary of information on each sample. This information included the sample identification, the date of collection, the type of sample or tissue, the species (for fish and mammals), 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
5182	R785A17	Environmental Trace Substances Research Center (ETSRC), Columbia, MO 65203
5431	R78725F	Research Triangle Institute (RTI) Cornwallis Road P.O. Box 12194 Research Triangle Park, NC 27709
5443	R78737F	Versar, Inc. 6850 Versar Center Springfield, VA 22151
5751	887116B	RTI
5754	887116A	Versar, Inc.

5957	897108	ETSRC
6407	907105	Hazleton Laboratories America, Inc. 3301 Kinsman Blvd. Madison, WI 53704
6455	907105B	RTI

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 PRESERVATION/STORAGE AND SHIPMENT

Samples for total metals, total recoverable metals, and dissolved metals analysis were acidified to a pH <2 with either 1-1.5 mL (1985) or 2-mL (1987, 1988) HNO_3 (Ultrix). All trace metal water samples were collected in new 500-mL acid-precleaned high-density polyethylene bottles from either the Environmental Protection Agency (EPA) (1985) or I-Chem (1987, 1988). Water, sediment, and fish samples were placed in coolers with ice, blue ice, or snow, and transported by boat or float plane to refrigerators for temporary storage. Water samples were refrigerated from the date of collection until shipment; sediment and fish tissues were kept frozen. Samples were shipped to the laboratory by air courier. Water samples were shipped with ice; frozen samples were shipped with dry ice.

SAMPLE HOLDING TIMES

Holding times for all catalogs exceeded the prescribed holding time for mercury in water which is 28 days; the maximum recommended holding time for other metals in water is 6 months (APHA et al. 1989). No holding times have been established for metals in sediments or tissues; however, it is widely assumed that loss from these media by volatilization or plating onto the container wall would be minimal. Based on the prolonged holding times, mercury is likely to have been lost from the water samples and those results are considered invalid. For other metals, particularly cadmium, significant losses may have also occurred.

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
CATNO	Catalog # and sequential #	5445-01	Assigned by Patuxent	Unique # for batch of samples
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
KA - Kanuti NWR

MR - Minto Flats
HR - Haul Road
SR - Sagavanirktok R
NS - Norton Sound
DP - Denali Park

YF - Yukon Flats NWR
CR - Chena River
KY - Koyukuk NWR

FA - Fairbanks
MI - Lake Minchumina
R - Yukon River
NA - North Slope (other)
TE - Tetlin NWR

SE - Selawik NWR
NO - Nowitna NWR
PB - Prudhoe Bay

DL - Delta
CO - Colville R.
PR - Porcupine R.

Species Codes

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

W - water
S - sediment, soil
V - vegetation

M - mammal
I - invertebrate
B - bird

F - fish

If the study involves known species, use these codes:

Fish

A - Arctic cisco
B - burbot
L - longnose sucker

M - humpback whitefish

H - chinook salmon

O - coho salmon

P - northern pike

I - chum salmon
K - Alaska blackfish
T - lake trout

U - slimy sculpin

W - round whitefish

Y - sockeye salmon

N - ninespine stickleback

R - broad whitefish
C - least cisco
D - Dolly Varden/charr

E - lake chub

F - sheefish

G - Arctic grayling

Birds

A - osprey

B - bald eagle
C - northern harrier

D - rough-legged hawk
E - golden eagle
F - phalarope

G - American kestrel

H - Merlin L - glaucous gull
I - peregrine falcon

J - gyrfalcon
K - boreal owl
L - glaucous gull

M - spectacled eider

O - oldsquaw
P - pectoral sandpiper

O - oldsquaw
R - rock
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 the Kanuti study were analyzed using a computor 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 (APHA et al. 1989). Depending on the laboratory performing the analyses, the LOD referenced could refer to the instrumental detection limit for a given sample, the typical "method" detection limit, the lower limit of detection for all samples, or the limit of quantitation, above which results can be viewed as semi-quantitative or quantitative. A general definition for LOD is that it is the lowest concentration level that can be distinguished statistically from a blank sample. That is, it is a reliable limit for an analyte, above which values are consistently detectable and distinguishable from instrument noise. Samples reported as being below the detection limit in a data set are generally reported as <X where X is the LOD. Occasionally, they may also be reported as ND (not detected), with the method LOD usually listed elsewhere in the catalog.

For analyses performed before 1989, the method of determining the LOD varied. In practice, contract laboratories usually adjusted the stated method LOD for typical percent moisture, sample size, and, if needed, chemical interferences. Individual sample LOD's may also be reported by the laboratory. These are generally shown adjacent to the measured concentration of an analyte in the sample. Because the method LOD actually varies depending on the nature of the individual sample, the upper LOD reported for each matrix in a sample catalog was adopted as the limit of detection for the QA-QC screening of the data.

ANALYTICAL PRECISION

Precision refers to the degree of agreement among repeated measurements of a given sample and is not a measure of accuracy. Precision varies with such factors as the homogeneity of the sample, sample volume, sample matrix, instrumental method, instrumental drift, chemical interferences, and the analyte concentration in the sample. Estimates of precision used for this study were made using duplicate analysis, where 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 (water, 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 (APHA et al. 1989). 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. In the QA-QC report, an asterisk is used to identify cases where the RPD cannot be calculated. For sample concentrations less than twice the 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 greater than 2(LOD) and less than 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 greater than 10(LOD), analyses can be expected to be highly quantitative. However, the same criterion, ±20%, is applied for screening data values both between greater than 2(LOD) and less than 10(LOD), and greater than 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.

The criteria selected for precision in the QA-QC computer program are not particularly rigorous. However, because water and soil samples from the sites were collected in triplicate, and multiple fish were collected per site, these criteria probably ensure adequate average precision for the prescribed use of the data.

ANALYTICAL ACCURACY

Spiked Samples

In addition to precision, measurements of correctness of the 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 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 greater than 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, rather than complete digestions; 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 APHA et al. (1989). 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 APHA et al. (1989) criteria for performance evaluation samples of water and wastewater.

Standard Reference Materials

Standard reference materials (SRM's) or interim reference materials 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), the Environmental Protection Agency (EPA), 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 the range of the certified value ± 3 SD, the SRM data are considered acceptable. A printout is also given of analytes for which the measured values fall outside ± 3 SD; these data are listed as questionable. On the QA-QC Summary Sheet for each catalog (Appendix D), "Low SRM" and "High SRM" show this confidence interval. Where the SRM SD is not known, it is defined as 10% of the certified value. Use of 10% as the estimated standard deviation is based on examination of the average relationship between the mean and standard deviation for several National Institute of Standards and Technology SRM's for a suite of metals. Typically, the standard deviation is 5 - 10% of the true value.

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) ± 3 SD. Occasionally this average measured SRM value is less than twice the LOD. In this case, "AvgSRM < 2 * LOD" appears on the QA-QC Summary Sheet. If two different SRM's are used for the same matrix and analytes, then each measured value is compared to the acceptable range for that SRM, and the SRM score is averaged. This score indicates how many SD's above or below the mean the measured value of the SRM falls. In the QA-QC Summary Sheet, the SRM score is given for each analyte by SRM. All SRM scores outside the range of the certified value ± 3 SD are also sorted to the "Questionable Quality Data" report.

BLANKS

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

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 the Kanuti 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 (RAW DATA)

Footnotes for QA-QC Screening Results are as follows:

[1] The average relative percent difference (RPD) from duplicate sample analyses, indicating precision. If the concentration of an analytical result is <2(LOD), then the measurement is considered imprecise, and "Qualitative only" is listed. RPDs >20% are unacceptable and are listed.

[2] The average percent spike recovery. Average spike recoveries <80% or >120% are condsidered unacceptable and are listed.

[3] The number of standard deviations (Z-score) that the measured SRM differed from the certified mean for that SRM. Z-scores >3 or <-3 are unacceptable. All Z-scores are listed.

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

Quality Assurance/Quality Control screening results are available at:

U.S. Fish and Wildlife Service
101 12th Ave.
Box 19, Room 110
Fairbanks, AK 99701

These data were not included with this document in an attempt to reduce the size of this file.

APPENDIX E: METALS IN WATER, 1987 (RAW DATA)

Table E-1. Total metal concentrations (mg/L) in water from Kanuti National Wildlife Refuge, Alaska, 1987.

				Metal Concentrations (mg/L)									
Site	Rep.	T	Date	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Tl	Zn
1	B	T	05/25	<0.005	0.001	<0.022	0.014	4.360	0.143	0.007	0.039	<0.05	0.021
1	C	T	05/25	<0.005	<0.001	<0.022	0.010	4.930	0.149	0.008	0.061	<0.05	0.027
2	B	T	05/26	<0.005	<0.001	<0.022	0.014	5.050	0.125	0.007	0.021	<0.05	0.021
2	C	T	05/26	<0.005	<0.001	<0.022	0.012	8.380	0.208	0.120	0.022	<0.05	0.033
3	B	T	05/26	<0.005	<0.001	<0.022	0.009	2.300	0.075	0.005	0.034	<0.05	0.011
3	C	T	05/26	<0.005	<0.001	<0.022	0.007	2.860	0.082	0.006	0.082	<0.05	0.018
4	B	T	05/26	<0.005	<0.001	<0.022	0.015	5.490	0.143	0.010	0.045	<0.05	0.020
4	C	T	05/26	<0.005	<0.001	<0.022	0.013	7.840	0.196	0.013	0.038	<0.05	0.031
5	C	T	05/27	<0.005	<0.001	<0.022	0.011	5.570	0.122	0.009	0.037	<0.05	0.020
6	B	T	05/27	<0.005	<0.001	<0.022	0.009	2.450	0.060	0.006	0.032	<0.05	0.012
6	C	T	05/27	<0.005	<0.001	<0.022	0.010	0.783	0.013	0.003	0.018	<0.05	0.011
7	C	T	05/27	<0.005	<0.001	<0.022	<0.01	1.810	0.054	0.005	0.034	<0.05	0.016
10	B	T	05/27	<0.005	<0.001	<0.022	0.008	0.627	0.030	0.004	0.028	<0.05	0.011
10	C	T	05/28	<0.005	<0.001	<0.022	0.006	0.732	0.035	0.006	0.036	<0.05	0.008

App. E Cont.

Site	Rep.	T	Date	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Tl	Zn
11	B	T	05/27	<0.005	<0.001	<0.022	0.001	0.549	0.027	0.007	0.028	<0.05	0.011
11	C	T	05/28	<0.005	<0.001	<0.022	0.005	0.510	0.024	0.009	0.035	<0.05	0.008
12	C	T	05/29	<0.005	<0.001	<0.022	0.009	1.170	0.041	0.004	0.032	<0.05	0.011
13	C	T	05/29	<0.005	<0.001	<0.022	0.008	0.537	0.020	0.004	0.057	<0.05	0.007

Table E-2. Total recoverable metal concentrations (mg/L) in water from Kanuti National Wildlife Refuge, Alaska, 1987.

				Metals Concentrations (mg/L)									
Site	Rep.	T	Date	As	Cd	Cr	Cu	Fe	Pb	Mn	NI	Tl	Zn
1	B	R	05/25	<0.005	<0.001	0.008	<0.007	4.160	0.026	0.147	0.007	<0.05	0.017
1	C	R	05/25	<0.005	0.002	0.017	0.007	4.040	0.026	0.133	0.015	<0.05	0.020
2	B	R	05/26	<0.005	<0.001	0.007	0.007	5.080	0.013	0.131	0.009	<0.05	0.020
2	C	R	05/26	<0.005	<0.001	0.013	0.009	7.160	0.017	0.197	0.017	<0.05	0.029
3	B	R	05/26	<0.005	<0.001	0.007	<0.007	2.180	0.023	0.066	0.006	<0.05	0.005
3	C	R	05/26	<0.005	<0.001	0.012	<0.007	2.840	0.025	0.084	0.008	<0.05	0.008
4	B	R	05/26	<0.005	<0.001	0.010	<0.007	5.490	0.031	0.130	0.009	<0.05	0.017
4	C	R	05/26	<0.005	<0.001	0.016	0.009	7.460	0.025	0.190	0.015	<0.05	0.019
5	C	R	05/27	<0.005	<0.001	0.015	<0.007	4.960	0.023	0.115	0.011	<0.05	0.018
6	B	R	05/27	<0.005	<0.001	<0.022	<0.007	2.240	0.020	0.057	<0.003	<0.05	0.008
6	C	R	05/27	<0.005	<0.001	0.008	<0.007	0.782	0.007	0.013	0.007	<0.05	0.006
7	C	R	05/27	<0.005	<0.001	<0.022	<0.007	1.790	0.024	0.053	0.017	<0.05	0.012
10	B	R	05/27	<0.005	<0.001	<0.022	<0.007	0.614	0.020	0.035	0.004	<0.05	0.005
10	C	R	05/28	<0.005	0.001	0.012	<0.007	0.970	0.027	0.031	0.010	<0.05	0.007
11	B	R	05/27	<0.005	<0.001	<0.022	<0.007	0.634	0.023	0.027	0.003	<0.05	0.010
11	C	R	05/28	<0.005	<0.001	0.024	<0.007	0.721	0.025	0.290	0.037	<0.05	<0.010
12	C	R	05/29	<0.005	0.005	0.135	0.017	1.700	0.038	0.076	0.098	<0.05	0.018
13	C	R	05/29	<0.005	<0.001	<0.022	<0.007	0.545	0.022	0.018	<0.003	<0.05	<0.010

Table E-3. Dissolved metal concentrations (mg/L) in water from Kanuti National Wildlife Refuge, Alaska, 1987.

				Metals Concentrations (mg/L)								
Site	Rep.	T	Date	As	Cr	Cu	Fe	Mn	Pb	Sn	Tl	Zn
1	A	D	05/25	<0.005	0.014	<0.07	0.101	0.024	0.044	0.010	<0.05	<0.01
1	B	D	05/25	<0.005	<0.022	<0.07	0.162	0.027	0.046	<0.01	<0.05	0.025
1	C	D	05/25	<0.005	<0.022	<0.07	0.181	0.039	0.069	<0.01	<0.05	0.022
2	A	D	05/26	<0.005	0.014	0.099	<0.101	0.019	0.040	0.010	<0.05	<0.01
2	B	D	05/25	<0.005	<0.022	<0.07	0.194	0.022	0.086	<0.01	<0.05	0.012
2	C	D	05/25	<0.005	<0.022	<0.07	0.259	0.024	0.047	<0.01	<0.05	0.015
3	A	D	05/26	<0.005	0.013	<0.07	0.242	0.019	0.061	0.402	<0.05	<0.01
3	B	D	05/26	<0.005	<0.022	<0.07	0.364	0.021	0.095	<0.01	<0.05	0.015
3	C	D	05/26	<0.005	<0.022	<0.07	0.380	0.024	0.080	0.083	<0.05	0.037
4	A	D	05/26	<0.005	0.016	<0.07	0.101	0.013	0.072	<0.01	<0.05	<0.01
4	B	D	05/26	<0.005	<0.022	<0.07	0.234	0.026	0.082	<0.01	<0.05	0.014
4	C	D	05/26	<0.005	<0.022	<0.07	0.195	0.018	0.054	<0.01	<0.05	<0.01
5	A	D	05/27	<0.005	0.018	<0.07	0.208	0.014	0.085	<0.01	<0.05	<0.01
5	B	D	05/27	<0.005	<0.022	<0.07	0.342	0.019	0.098	<0.01	<0.05	0.013
5	C	D	05/27	<0.005	<0.022	<0.07	0.309	0.017	0.079	<0.01	<0.05	0.022

Dissolved metals continued

Site	Rep.	T.	Date	As	Cr	Cu	Fe	Mn	Pb	Sn	Tl	Zn
6	A	D	05/27	<0.005	0.016	<0.07	0.443	0.020	0.066	<0.01	<0.05	<0.01
6	B	D	05/27	<0.005	<0.022	<0.07	1.060	0.038	0.080	<0.01	<0.05	0.019
6	C	D	05/27	<0.005	<0.022	<0.07	0.570	0.029	0.099	<0.01	<0.05	0.015
7	A	D	05/27	<0.005	0.016	<0.07	0.169	0.011	0.077	<0.01	<0.05	<0.01
7	B	D	05/27	<0.005	<0.022	<0.07	0.272	0.016	0.086	<0.01	<0.05	0.013
7	C	D	05/27	<0.005	<0.022	<0.07	0.262	0.016	0.082	<0.01	<0.05	0.015
10	A	D	05/28	<0.005	0.016	0.098	<0.101	0.007	0.071	<0.01	<0.05	<0.01
10	B	D	05/28	<0.005	<0.022	<0.07	0.170	0.012	0.064	<0.01	<0.05	<0.01
10	C	D	05/28	<0.005	<0.022	<0.07	0.255	0.011	0.061	<0.01	<0.05	0.013
11	A	D	05/28	<0.005	0.013	<0.07	<0.101	0.006	0.045	<0.01	<0.05	<0.01
11	B	D	05/28	<0.005	<0.022	<0.07	0.169	0.012	0.072	<0.01	<0.05	<0.01
11	C	D	05/28	<0.005	<0.022	<0.07	0.169	0.012	0.076	<0.01	<0.05	0.014
12	A	D	05/29	<0.005	0.012	<0.07	<0.101	0.008	0.054	<0.01	<0.05	<0.01
12	B	D	05/28	<0.005	0.018	<0.07	0.130	0.013	0.076	<0.01	<0.05	<0.01
12	C	D	05/29	<0.005	<0.022	<0.07	0.188	0.010	0.058	<0.01	<0.05	<0.01
13	A	D	05/28	<0.005	0.014	<0.07	0.157	0.008	0.057	<0.01	<0.05	<0.01
13	B	D	05/29	<0.005	0.022	<0.07	0.170	0.010	0.089	<0.01	<0.05	<0.01
13	B	D	05/29	<0.005	0.012	<0.07	0.538	0.020	0.017	<0.01	<0.05	0.313
13	C	D	05/29	<0.005	<0.022	<0.07	0.262	0.012	0.055	<0.01	<0.05	0.019

APPENDIX F: METALS IN WATER, 1988 (RAW DATA)

Total recoverable and dissolved metal concentrations (mg/L) in water from Kanuti National Wildlife Refuge, Alaska, 1988.

Site	Rep.	Mn[a]	Ni[a]	Pb[b]
02	A	-[c]	0.01	0.027
02	B	-	0.02	0.026
02	C	-	<0.01	0.033
20	A	-	<0.01	0.041
20	B	-	<0.01	0.039
20	C	0.09	<0.01	0.033
22	A	0.02	<0.01	0.040
22	B	0.03	<0.01	0.047
22	C	0.03	<0.01	0.048
23	A	0.05	<0.01	0.042
23	B	0.06	<0.01	0.033
23	C	-	<0.01	0.032
24	A	-	<0.01	0.041
24	B	0.06	<0.01	0.032
24	C	-	<0.01	0.049
25	A	0.09	<0.01	0.054
25	B	-	<0.01	<0.015
25	C	0.09	<0.01	0.031
26	A	0.06	<0.01	0.046
26	B	0.06	<0.01	0.055
26	C	-	<0.01	0.041

[a] Total recoverable metal. [b] Dissolved metal. [c] A dash (-) indicates that the measured value was greater than the total metals value.

APPENDIX G: SEDIMENT, 1987 (RAW DATA)

Metal concentrations in sediment from Kanuti National Wildlife Refuge, Alaska, 1987.

			Metals Concentrations (mg/kg dry weight)									
Site	Rep.	Date	As	Ba	Be	Cr	Cu	Pb	Mn	Ni	Sr	Zn
01	A	05/25	7.60	28.00	0.17	13.00	34.00	7.40	693	28.0	83.0	87.0
01	B	05/25	6.90	29.00	<0.17	14.00	35.00	5.00	723	29.0	88.0	93.0
01	C	05/25	8.10	28.00	<0.17	13.00	32.00	10.00	701	26.0	96.0	87.0
Mean[a]			7.53	28.33		13.33	33.67	7.47	706	27.7	89.0	89.0
02	A	05/26	4.70	20.00	<0.17	12.00	17.00	8.60	420	21.0	44.0	56.0
02	B	05/26	7.80	30.00	0.19	13.00	29.00	9.10	578	26.0	57.0	80.0
02	C	05/26	5.80	18.00	0.19	9.50	18.00	5.20	448	18.0	50.0	53.0
Mean			6.10	22.67	0.15	11.50	21.33	7.63	482	21.7	50.3	63.0
03	A	05/26	2.70	48.00	<0.17	9.60	11.00	<5.00	428	14.0	9.4	40.0
03	B	05/26	3.90	94.00	0.22	17.00	21.00	<5.00	360	20.0	15.0	57.0
03	C	05/26	2.20	31.00	<0.17	6.70	9.20	<5.00	409	10.0	5.0	26.0
Mean			2.93	57.67		11.10	13.73		399	14.7	9.8	41.0

Appendix G Cont.

Site	Rep.	Date	As	Ba	Be	Cr	Cu	Pb	Mn	Ni	Sr	Zn
04	A	05/26	6.10	27.00	<0.17	14.00	27.00	9.70	581	27.0	68.0	78.0
04	B	05/26	5.90	22.00	<0.17	12.00	22.00	7.70	513	23.0	69.0	70.0
04	C	05/26	4.80	21.00	0.15	2.00	18.00	9.70	450	22.0	58.0	62.0
Mean			5.60	23.33		2.67	22.33	9.03	515	24.0	65.0	70.0
05	A	05/27	2.80	56.00	<0.17	11.00	12.00	<5.00	278	15.0	12.0	38.0
05	B	05/27	3.50	67.00	<0.17	14.00	14.00	<5.00	316	17.0	15.0	44.0
05	C	05/27	3.50	73.00	<0.17	14.00	15.00	<5.00	358	19.0	15.0	48.0
Mean			3.27	65.33		13.00	13.67		317	17.0	14.0	43.3
06	A	05/27	3.10	52.00	0.18	12.00	9.00	5.50	217	13.0	9.6	41.0
06	B	05/27	4.00	90.00	<0.17	17.00	15.00	6.10	338	19.0	16.0	60.0
06	C	05/27	5.40	123.00	0.33	21.00	21.00	<5.00	468	23.0	22.0	75.0
Mean			4.17	88.33	0.19	16.67	15.00	4.70	341	18.3	15.9	58.7
07	A	05/27	5.00	100.00	<0.17	18.00	25.00	<5.00	483	23.0	22.0	53.0
07	B	05/27	3.00	59.00	<0.17	14.00	16.00	<5.00	292	18.0	15.0	41.0
07	C	05/27	3.90	78.00	0.17	15.00	20.00	<5.00	372	19.0	17.0	51.0
Mean			3.97	79.00		15.67	20.33		382	20.0	18.0	48.3

Appendix G Continued

Site	Rep.	Date	As	Ba	Be	Cr	Cu	Pb	Mn	Ni	Sr	Zn
10	A	05/28	6.20	60.00	<0.17	13.00	18.00	<5.00	414	20.0	17.0	52.0
10	B	05/28	4.80	52.00	0.17	13.00	17.00	5.70	390	20.0	14.0	48.0
10	C	05/28	5.50	73.00	<0.17	14.00	20.00	<5.00	459	22.0	22.0	58.0
Mean			5.50	61.67		3.33	18.33		421	20.7	17.7	52.7
11	A	05/28	5.20	61.00	<0.17	16.00	21.00	<5.00	397	21.0	21.0	56.0
11	B	05/28	5.40	44.00	<0.17	12.00	14.00	6.40	371	18.0	11.0	40.0
11	C	05/28	4.30	53.00	0.17	11.00	17.00	<5.00	351	18.0	13.0	44.0
Mean			4.97	52.67		13.00	17.33		373	19.0	15.0	46.7
12	A	05/29	5.80	57.00	<0.17	15.00	17.00	7.00	418	20.0	14.0	50.0
12	B	05/29	6.90	55.00	<0.17	13.00	17.00	<5.00	395	19.0	15.0	48.0
12	C	05/29	3.80	46.00	0.17	13.00	15.00	<5.00	371	19.0	11.0	41.0
Mean			5.50	52.67		13.67	16.33		395	19.3	13.3	46.3
13	A	05/29	4.80	79.00	<0.17	12.00	20.00	<5.00	468	18.0	12.0	43.0
13	B	05/29	5.80	111.00	<0.17	15.00	20.00	<5.00	498	18.0	15.0	51.0
13	C	05/29	4.10	82.00	0.18	13.00	21.00	<5.00	564	18.0	12.0	47.0
Mean			4.90	90.67		13.33	20.33		510	18.0	13.0	47.0

[a] - Where concentrations of two or three replicates were <LOD, means were not calculated; when ony one replicate was <LOD, a value of one-half of the LOD was used for that replicate in calculation of the mean. LODs (mg/kg-dry weight) were as follows: As 0.80, Ba 3.0, Be 0.20, Cr 0.30, Cu 0.50, Pb 5.0, Mn 0.20, Ni 2.0, Sr 1.0, Zn 0.20.

APPENDIX H: SEDIMENT, 1988 (RAW DATA)

Metal concentrations in sediment from Kanuti National Wildlife Refuge, Alaska, 1988.

			Metals Concentrations (mg/kg dry weight)												
Site	Rep.	Date	As	Ba	Be	Cd	Cu	Fe	Pb	Ni	Sr	Sn	Tl	V	Zn
2	A	08/22	12.2	36.0	0.17	0.50	28.0	29800	11.2	32.8	76.0	9.1	325	17.1	89.0
2	B	08/22	9.7	35.5	0.15	<0.50	27.6	28900	11.1	32.0	72.3	8.3	345	16.0	86.3
2	C	08/22	7.1	35.8	0.21	<0.50	27.1	28500	13.6	32.4	72.6	10.6	320	15.6	85.1
Mean[a]			9.7	35.8	0.18		27.6	29067	12.0	32.4	73.6	9.3	330	16.2	86.8
20	A	08/22	8.2	32.6	0.24	0.50	26.4	32300	13.1	35.5	53.6	10.2	364	15.8	92.6
20	B	08/22	<5.00	33.2	0.25	0.50	26.9	32600	12.9	35.2	52.9	10.0	357	15.8	91.8
20	C	08/22	5.6	32.4	0.20	<0.50	26.2	32100	12.5	35.7	52.2	8.9	319	15.3	90.2
Mean			5.4	32.7	0.23	0.42	26.5	32333	12.8	35.5	52.9	9.7	347	15.6	91.5
22	A	08/22	16.0	42.1	0.24	0.65	36.7	32700	15.5	39.7	80.3	9.3	377	22.2	114.0
22	B	08/22	11.1	38.2	0.17	0.59	34.6	30100	12.9	35.9	78.1	7.2	332	19.1	104.0
22	C	08/22	13.2	43.4	0.21	0.68	37.2	31600	15.2	37.0	76.7	10.0	354	21.4	109.0
Mean			13.4	41.2	0.21	0.64	36.2	31467	14.5	37.5	78.4	8.8	354	20.9	109.0

Appendix H Continued

Site	Rep.	Date	As	Ba	Be	Cd	Cu	Fe	Pb	Ni	Sr	Sn	Tl	V	Zn
23	A	08/23	11.1	28.3	0.22	0.73	25.6	27300	10.1	31.5	103.0	11.4	297	16.0	81.7
23	B	08/23	11.3	20.7	0.13	<0.50	23.3	26300	10.8	30.2	86.2	9.3	292	15.2	75.7
23	C	08/23	8.6	22.3	0.19	0.55	24.7	24800	9.6	29.1	100.0	9.7	280	13.6	74.9
Mean			10.3	23.8	0.18	0.51	24.5	26133	10.2	30.3	96.4	10.1	290	14.9	7.4
24	A	08/23	9.1	22.8	0.17	0.63	29.8	28200	14.4	32.4	87.6	14.9	300	18.1	103.0
24	B	08/23	10.2	24.1	0.18	<0.50	28.9	27800	10.6	32.8	96.2	10.0	318	16.4	102.0
24	C	08/23	10.3	24.5	0.15	0.51	29.9	29000	9.9	34.4	98.5	8.3	330	18.1	111.0
Mean			9.9	23.8	0.17	0.46	29.5	28333	11.6	33.2	94.1	11.1	316	17.5	105.3
25	A	08/23	9.6	25.6	0.17	<0.50	28.9	27100	10.6	29.3	147.0	10.8	322	14.8	76.6
25	B	08/23	10.4	28.9	0.22	0.71	29.0	29500	12.1	31.6	132.0	11.7	330	15.5	84.4
25	C	08/23	9.1	28.3	0.24	<0.50	28.3	30200	12.1	32.5	134.0	11.1	340	16.4	83.4
Mean			9.7	27.6	0.21		28.7	28933	11.6	31.1	137.7	11.2	331	15.6	81.5
26	A	08/23	11.3	16.9	0.17	<0.50	25.3	25800	11.4	28.9	146.0	9.3	290	14.0	71.7
26	B	08/23	8.2	22.8	0.21	<0.50	25.8	26800	11.5	29.1	140.0	10.5	312	14.6	75.6
26	C	08/23	14.3	22.2	0.20	<0.50	26.6	26200	10.5	28.9	143.0	9.9	287	14.6	74.2
Mean			11.3	20.6	0.19		25.9	26267	11.1	29.0	143.0	9.9	296	14.4	73.8

[a] - Where concentrations of two or three replicates were <LOD, means were not calculated; when ony one replicate was <LOD, a value of one-half of the LOD was used for that replicate in calculation of the mean. LODs (mg/kg-dry weight) were as follows: As 1.0, Ba 0.5, Be 0.1, Cd 0.5, Cu 0.5, Fe 10, Pb 5.0, Mo 1.0, Ni 2.0, Sn 10, Sr 1.0, Tl 10, V 1.0, Zn 1.0.

APPENDIX I: FISH TISSUE, 1987 (RAW DATA)

Metals concentrations of kidney, liver, muscle and whole body (mg/kg dry weight), and total length (mm), fork length (mm) and weight (gm) of Arctic grayling (*Thymallus arcticus*), longnose sucker (*Catastomus catastomus*), and northern pike (*Esox lucius*) collected from Kanuti National Wildlife Refuge, Alaska, 1987.

					Metals Concentrations (mg/kg dry weight)							
Site	Rep.	Species[a]	Tissue[b]	Date	Cd	Co	Cr	Ni	Hg	T.L.[c]	F.L.[c]	WT.[c]
1	A	LS	K	05/25	<0.20	<0.50	<0.62	1.15	-	42.1	39.5	600
1	A	LS	L	05/25	1.97	<0.50	0.87	1.10	0.08	42.1	39.5	600
1	A	LS	M	05/25	<0.20	<0.50	<0.62	<0.80	0.45	42.1	39.5	600
1	B	LS	K	05/26	5.54	<0.50	<0.62	2.47	-	41.8	39.5	652
1	B	LS	L	05/26	1.41	<0.50	<0.62	<0.80	<0.02	41.8	39.5	652
1	B	LS	M	05/26	<0.20	<0.50	<0.62	<0.80	0.21	41.8	39.5	652
1	C	LS	M	05/26	<0.20	<0.50	<0.62	<0.80	0.49	39.8	37.7	540
1	D	LS	L	05/26	0.48	<0.50	<0.62	1.27	-	42.5	40.2	812
1	D	LS	M	05/26	<0.20	<0.50	<0.62	<0.80	0.60	42.5	40.2	812
1	A	NP	K	05/25	7.61	<0.50	<0.62	3.93	0.36	54.5	51.6	907
1	A	NP	L	05/25	0.20	<0.50	1.02	<0.80	0.19	54.5	51.6	907
1	A	NP	M	05/25	<0.20	<0.50	<0.62	2.46	0.64	54.5	51.6	907
1	B	NP	K	05/25	2.48	0.52	<0.62	14.40	0.21	51.4	48.5	768
1	B	NP	L	05/25	<0.20	<0.50	0.96	<0.80	0.09	51.4	48.5	768
1	B	NP	M	05/25	<0.20	<0.50	<0.62	<0.80	0.48	51.4	48.5	768
2	A	AG	W	05/26	<0.20	<0.50	0.80	0.80	0.26	34.9	32.5	322
2	B	AG	W	05/26	0.12	<0.50	0.94	0.80	0.22	33.2	30.9	301
2	C	AG	W	05/26	<0.20	<0.50	0.75	<0.80	0.27	30.5	28.0	227

Appendix I continued

Site	Rep.	Species	Tissue	Date	Cd	Co	Cr	Ni	Hg	T.L.	F.L.	WT.
2	D	AG	W	05/26	<0.20	<0.50	0.79	<0.80	0.25	29	26.8	181
2	E	AG	W	05/26	<0.20	0.45	0.92	<0.80	0.22	29.3	26.9	176
3	A	AG	W	05/26	<0.20	<0.50	<0.62	<0.80	0.16	36.8	34.0	369
3	B	AG	W	05/26	<0.20	<0.50	0.86	<0.80	0.19	40.6	37.3	506
3	C	AG	W	05/27	0.20	<0.50	1.30	<0.80	0.21	33.4	30.8	313
3	D	AG	W	05/27	<0.20	<0.50	0.89	<0.80	0.44	37.3	34.5	390
3	E	AG	W	05/27	<0.20	<0.50	0.70	<0.80	0.23	38.2	35.3	384
3	A	LS	K	05/27	10.70	<0.50	<0.62	<0.80	-	42.8	40.4	719
3	A	LS	L	05/27	3.62	<0.50	<0.62	<0.80	0.16	42.8	40.4	719
3	A	LS	M	05/27	<0.20	<0.50	<0.62	<0.80	0.74	42.8	40.4	719
3	B	LS	K	05/27	3.96	0.91	2.72	4.64	-	39.3	37.3	515
3	B	LS	L	05/27	0.69	<0.50	0.95	1.21	-	39.3	37.3	515
3	B	LS	M	05/27	0.20	<0.50	<0.62	<0.80	0.84	39.3	37.3	515
3	C	LS	K	05/27	4.51	<0.50	0.74	1.28	-	38.7	36.3	518
3	C	LS	L	05/27	1.81	<0.50	0.79	<0.80	0.11	38.7	36.3	518
3	C	LS	M	05/27	<0.20	0.63	0.71	1.46	0.66	38.7	36.3	518
3	A	NP	L	05/26	<0.20	<0.50	<0.62	<0.80	0.22	42.1	39.5	445
3	A	NP	M	05/26	<0.20	<0.50	<0.62	<0.80	1.55	42.1	39.5	445
3	B	NP	K	05/27	0.42	<0.50	<0.62	<0.80	1.49	68.9	65.8	1950
3	B	NP	L	05/27	0.20	<0.50	<0.62	<0.80	0.51	68.9	65.8	1950
3	B	NP	M	05/27	0.20	<0.50	<0.62	<0.80	1.85	68.9	65.8	1950
3	C	NP	K	05/27	1.16	<0.50	0.65	3.10	2.28	60.1	56.7	1250
3	C	NP	L	05/27	<0.20	0.59	<0.62	1.17	0.72	60.1	56.7	1250

Appendix I continued

Site	Rep.	Species	Tissue	Date	Cd	Co	Cr	Ni	Hg	T.L.	F.L.	WT.
3	C	NP	M	05/27	<0.20	<0.50	<0.62	1.11	2.11	60.1	56.7	1250
3	D	NP	K	05/27	0.79	<0.50	<0.62	1.99	1.29	53.6	50.7	896
3	D	NP	L	05/27	<0.20	<0.50	<0.62	0.95	0.46	53.6	50.7	896
3	D	NP	M	05/27	<0.20	<0.50	<0.62	1.48	1.43	53.6	50.7	896
5	A	AG	W	05/28	0.20	<0.50	0.86	1.04	0.16	34.9	32.5	322
5	B	AG	W	05/28	0.21	<0.50	1.12	1.19	0.28	33.2	30.9	301
5	C	AG	W	05/28	<0.20	<0.50	0.91	1.33	0.59	30.5	28.0	227
5	D	AG	W	05/27	<0.20	<0.50	<0.62	<0.80	2.03	29.0	26.8	181
5	E	AG	W	05/27	0.30	<0.50	0.76	1.03	1.61	39.3	26.9	176
6	A	LS	K	05/27	9.62	<0.50	<0.62	4.17	0.34	45.2	42.3	857
6	A	LS	L	05/27	2.60	<0.50	<0.62	1.42	0.20	45.2	42.3	857
6	A	LS	M	05/27	<0.20	<0.50	<0.62	0.83	1.20	45.2	42.3	857
6	B	LS	K	05/27	5.88	0.55	0.83	3.62	-	44.5	42.4	943
6	B	LS	L	05/27	1.70	<0.50	<0.62	3.06	0.19	44.5	42.4	943
6	B	LS	M	05/27	<0.20	<0.50	0.94	1.08	1.05	44.5	42.4	943
6	C	LS	K	05/27	1.14	<0.50	0.84	<0.80	-	53.7	50.5	1475
6	C	LS	L	05/27	0.54	<0.50	0.71	<0.80	0.08	53.7	50.5	1475
6	C	LS	M	05/27	<0.20	<0.50	<0.62	<0.80	0.24	53.7	50.5	1475
7	A	AG	W	05/27	<0.20	<0.50	0.86	0.92	0.16	25.8	23.5	
7	B	AG	L	05/27	0.34	<0.50	0.86	1.10	0.21	37.1	35.5	447
7	B	AG	M	05/27	<0.20	<0.50	<0.62	<0.80	0.20	37.1	35.5	447
7	C	AG	W	05/27	<0.20	0.99	0.73	<0.80	0.32	37.9	34.9	421
7	D	AG	W	05/27	<0.20	<0.50	1.20	1.00	0.15	35.6	33.1	346

Appendix I continued

Site	Rep.	Species	Tissue	Date	Cd	Co	Cr	Ni	Hg	T.L.	F.L.	WT.
7	E	AG	W	05/27	<0.20	<0.50	<0.62	<0.80	0.89	36.8	33.8	388
7	F	AG	W	05/27	<0.20	<0.50	1.18	<0.80	0.33	34.2	31.3	340
10	A	AG	W	05/28	<0.20	1.26	0.73	<0.80	0.27	32.6	30.2	253
10	B	AG	W	05/28	<0.20	0.80	0.86	12.40	0.30	30.1	28.1	234
10	C	AG	W	05/28	1.11	0.65	0.72	0.81	0.19	29.5	27.3	223
10	D	AG	W	05/28	0.38	0.68	1.69	2.21	0.18	28.8	26.5	189
10	E	AG	W	05/28	<0.20	<0.50	0.71	3.24	0.26	30.9	28.4	225
11	A	AG	W	05/28	<0.20	<0.50	<0.62	<0.80	0.12	22.7	21.0	88
11	B	AG	W	05/28	<0.20	1.29	0.76	<0.80	0.15	36.8	34.1	376
11	C	AG	W	05/28	0.32	<0.50	<0.62	2.20	0.22	30.0	27.7	221
12	A	AG	W	05/29	<0.20	<0.50	<0.62	2.14	0.17	31.6	29.3	241
12	B	AG	W	05/29	1.09	2.32	0.83	0.96	0.20	30.5	28.0	204
12	C	AG	W	05/29	<0.20	1.58	0.72	0.87	0.21	29.2	27.1	191
12	D	AG	W	05/29	<0.20	<0.50	1.21	1.97	0.17	28.8	26.4	200
12	E	AG	W	05/29	<0.20	<0.50	0.93	1.89	0.22	29.3	26.9	186
13	A	AG	L	05/29	0.41	0.94	<0.62	1.42	0.49	37.7	35.5	480
13	A	AG	M	05/29	<0.20	<0.50	<0.62	1.74	0.25	37.7	35.5	480
13	B	AG	W	05/29	<0.20	<0.50	1.41	0.83	0.20	38.0	35.2	420
13	C	AG	W	05/29	<0.20	0.64	1.15	1.53	0.18	34.6	32.0	369
13	D	AG	W	05/29	<0.20	0.97	<0.62	<0.80	0.13	30.0	28.1	234
13	E	AG	W	05/29	<0.20	<0.50	<0.62	0.87	0.08	33.2	31.2	223

[a] AG = Arctic Grayling, LS = Longnose Sucker, NP = Northern Pike.
[b] K = Kidney, L = Liver, M = Muscle. [c] T.L. = Total Length, F.L. = Fork Length, WT. = Weight;
Total length, fork length, and weight were measured approximately one-year after the samples were frozen and as a result, these measurements are likely less accurate.

APPENDIX J: FISH TISSUE, 1988 (RAW DATA)

Metals concentrations of kidney, liver, muscle and whole body, and total length (mm), fork length (mm) and weight (gm) of Arctic grayling (*Thymallus arcticus*), longnose sucker (*Catastomus catastomus*), and northern pike (*Esox lucius*) collected from Kanuti National Wildlife Refuge, Alaska, 1988.

					Metals Concentrations (mg/kg dry weight)									
Site	Rep.	S[a]	T[b]	Date	As	Ba	Be	B	Cd	Cr	Cu	Fe	Hg	Mg
1	A	AG	K	08/28	<0.20	<1.00	<0.10	<0.50	8.55	0.68	6.82	621	0.805	529
1	A	AG	L	08/28	0.23	<1.00	<0.10	0.55	3.08	<0.60	8.57	193	0.701	1030
1	A	AG	M	08/28	0.16	<1.00	<0.10	<0.50	<0.60	<0.60	3.06	<30	0.598	1220
1	B	AG	K	08/28	0.33	<1.00	<0.10	0.73	5.90	0.86	6.66	1060	0.997	614
1	B	AG	L	08/28	<0.20	<1.00	<0.10	<0.50	2.99	0.70	18.70	332	0.639	977
1	B	AG	M	08/28	0.36	1.25	<0.10	0.97	<0.60	<0.60	<2.00	<30	0.720	1320
1	A	LS	K	08/28	0.30	1.02	<0.10	<0.50	12.00	<0.60	5.22	542	0.055	539
1	A	LS	L	08/28	0.28	<1.00	<0.10	0.64	1.58	<0.60	29.70	365	0.100	715
1	A	LS	M	08/28	0.21	<1.00	<0.10	0.69	<0.60	0.64	2.76	<30	0.039	1460
1	B	LS	K	08/28	0.34	1.49	<0.10	0.63	102.00	0.77	8.17	825	1.170	739
1	B	LS	L	08/28	0.44	<1.00	<0.10	2.70	6.60	0.61	54.20	2800	0.535	753
1	B	LS	M	08/28	0.43	<1.00	0.18	1.38	<0.60	0.74	4.13	88	1.730	1270
1	C	LS	K	08/28	0.26	1.07	<0.10	<0.50	33.10	0.67	10.10	414	<0.200	684
1	C	LS	L	08/28	0.48	<1.00	0.35	0.75	4.82	1.06	44.20	636	0.072	723
1	C	LS	M	08/28	0.22	<1.00	<0.10	<0.50	<0.60	<0.60	2.61	34	0.236	1300
1	A	NP	K	08/28	<0.2	<1.00	<0.10	<0.50	2.73	<0.60	5.83	321	<0.200	<836
1	A	NP	L	08/28	<0.2	<1.00	<0.10	<0.50	<0.60	<0.60	3.86	75	<0.200	458
1	A	NP	M	08/28	<0.2	<1.00	<0.10	<0.50	<0.60	<0.60	15.30	<30	0.468	1590

Appendix J continued

Site	Rep.	S	T	Date	As	Ba	Be	B	Cd	Cr	Cu	Fe	Hg	Mg
1	B	NP	K	08/28	0.21	<1.00	0.17	1.17	3.01	0.82	6.41	463	0.303	858
1	B	NP	L	08/28	<0.20	<1.00	<0.10	<0.50	<0.60	<0.60	6.99	252	0.384	548
1	B	NP	M	08/28	<0.20	<1.00	0.12	1.08	<0.60	0.64	<2.00	<30	0.438	1590
1	C	NP	K	08/28	<0.20	<1.00	<0.10	<0.50	3.40	0.96	7.98	408	0.331	858
1	C	NP	L	08/28	<0.20	<1.00	<0.10	0.71	<0.60	<0.60	15.70	153	0.217	652
1	C	NP	M	08/28	<0.20	<1.00	0.29	0.72	<0.60	0.93	<2.00	<30	0.556	1530
1	D	NP	K	08/28	<0.20	<1.00	<0.10	<0.50	4.64	<0.60	23.80	439	<0.200	855
1	D	NP	L	08/28	<0.20	<1.00	<0.10	<0.50	<0.60	<0.60	17.20	127	0.174	618
1	D	NP	M	08/28	<0.20	<1.00	<0.10	<0.50	<0.60	<0.60	2.60	<30	0.461	1550
1	E	NP	K	08/28	<0.20	<1.00	<0.10	<0.50	3.64	<0.60	6.60	198	0.462	834
1	E	NP	L	08/28	<0.20	<1.00	<0.10	0.84	<0.60	0.61	11.47	189	0.209	641
1	E	NP	M	08/28	0.22	<1.00	<0.10	<0.50	<0.60	<0.60	<2.00	<30	0.448	1450
1	F	NP	W	08/28	<0.20	<1.00	<0.10	<0.50	<0.60	0.61	2.11	44	0.360	1090
1	G	NP	W	08/28	<0.20	1.61	<0.10	0.54	<0.60	1.28	2.59	64	0.297	1530
20	A	LS	K	08/18	0.29	<1.00	<0.10	0.60	1.01	1.35	3.18	310	0.028	1140
20	A	LS	L	08/18	0.59	<1.00	<0.10	0.99	2.83	<0.60	65.20	442	0.040	775
20	A	LS	M	08/18	0.34	<1.00	<0.10	<0.50	<0.60	<0.60	<2.00	<30	0.207	1340
22	A	AG	W	08/19	0.47	1.93	<0.10	<0.50	<0.60	1.46	5.27	81	0.059	1290
22	B	AG	W	08/19	0.27	2.18	<0.10	<0.50	<0.60	1.44	5.39	131	0.166	1370
22	C	AG	W	08/19	0.50	4.02	<0.10	1.18	<0.60	1.73	4.03	131	<0.200	1490
22	D	AG	L	08/19	0.25	<1.00	<0.10	2.18	4.24	<0.60	16.10	547	1.540	698

Appendix J continued

Site	Rep.	S	T	Date	As	Ba	Be	B	Cd	Cr	Cu	Fe	Hg	Mg
22	D	AG	M	08/19	0.53	<1.00	<0.10	<0.50	<0.60	<0.60	2.66	<30	0.313	1240
22	E	AG	W	08/19	<0.02	2.02	<0.10	<0.50	<0.60	1.09	2.57	107	0.166	1320
22	A	NP	K	08/18	0.29	1.30	<0.10	<0.50	1.76	0.88	7.97	473	0.131	836
22	A	NP	L	08/18	<0.2	<1.00	<0.10	<0.50	<0.60	<0.60	7.61	185	0.361	317
22	A	NP	M	08/18	0.27	<1.00	<0.10	<0.50	<0.60	0.62	<2.00	<30	0.516	1550
22	B	NP	L	08/19	<0.2	<1.00	<0.10	<0.50	<0.60	<0.60	12.40	182	<0.200	597
22	B	NP	M	08/19	0.21	<1.00	0.11	0.92	<0.60	<0.60	2.68	<30	<0.200	1600
23	A	AG	W	08/23	0.60	<1.00	<0.10	0.83	<0.60	4.93	5.08	301	0.373	975
23	A	LS	K	08/25	0.50	1.20	<0.10	<0.50	20.30	0.61	7.34	192	0.869	585
23	A	LS	L	08/25	0.33	<1.00	0.10	0.99	2.23	<0.60	27.70	362	0.234	<836
23	A	LS	M	08/25	0.52	<1.00	<0.10	<0.50	<0.60	0.85	3.39	<30	0.068	1460

Appendix J continued

Site	Rep.	S	T	Date	Mn	Ni	Pb	Se	Sr	V	Zn	T.L.[c]	F.L.[c]	WT.[c]
1	A	AG	K	08/28	<2.00	16.60	0.60	15.10	<3.00	1.84	80.5	353	319	355
1	A	AG	L	08/28	13.80	<3.50	2.21	7.87	<3.00	<0.50	156.0	353	319	355
1	A	AG	M	08/28	<2.00	<3.50	1.80	1.40	<3.00	<0.50	85.6	353	319	355
1	B	AG	K	08/28	<2.00	<3.50	0.40	26.40	<3.00	11.50	86.7	365	335	375
1	B	AG	L	08/28	<2.00	<3.50	0.37	7.27	<3.00	1.06	100.0	365	335	375
1	B	AG	M	08/28	<2.00	<3.50	0.25	1.42	5.94	<0.50	20.2	365	335	375
1	A	LS	K	08/28	4.34	<3.50	0.46	2.39	<3.00	0.70	170.0	356	335	450
1	A	LS	L	08/28	7.00	<3.50	0.43	3.51	<3.00	0.57	169.0	356	335	450
1	A	LS	M	08/28	<2.00	<3.50	0.31	1.53	<3.00	<0.50	32.9	356	335	450
1	B	LS	K	08/28	5.27	7.38	1.60	5.80	<3.00	<0.50	269.0	420	387	540
1	B	LS	L	08/28	4.73	<3.50	0.52	4.28	<3.00	<0.50	98.6	420	387	540
1	B	LS	M	08/28	9.58	<3.50	0.24	1.63	3.97	<0.50	51.7	420	387	540
1	C	LS	K	08/28	4.96	7.99	0.43	3.97	<3.00	<0.50	229.0	425	399	580
1	C	LS	L	08/28	8.82	<3.50	1.77	4.18	<3.00	0.71	88.2	425	399	580
1	C	LS	M	08/28	<2.00	<3.50	0.50	1.45	<3.00	<0.50	42.5	425	399	580
1	A	NP	K	08/28	4.58	<3.50	<0.21	6.76	<3.00	<0.50	219.0	436	411	520
1	A	NP	L	08/28	3.39	<3.50	0.28	4.37	<3.00	<0.50	61.9	436	411	520
1	A	NP	M	08/28	2.71	<3.50	<0.21	2.01	<3.00	<0.50	17.2	436	411	520
1	B	NP	K	08/28	4.21	<3.50	<0.21	4.48	<3.00	<0.50	190.0	474	450	675
1	B	NP	L	08/28	3.28	<3.50	0.23	3.75	<3.00	<0.50	86.3	474	450	675
1	B	NP	M	08/28	5.26	<3.50	0.21	1.40	<3.00	<0.50	17.2	474	450	675

Appendix J continued

Site	Rep.	S	T	Date	Mn	Ni	Pb	Se	Sr	V	Zn	T.L.	F.L.	WT.
1	C	NP	K	08/28	4.19	<3.50	<0.21	3.66	<3.00	<0.50	305.0	535	509	1075
1	C	NP	L	08/28	4.56	<3.50	0.44	3.32	<3.00	<0.50	108.0	535	509	1075
1	C	NP	M	08/28	2.00	<3.50	1.53	0.71	<3.00	<0.50	15.1	535	509	1075
1	D	NP	K	08/28	4.63	<3.50	<0.21	7.98	<3.00	<0.50	303.0	457	434	625
1	D	NP	L	08/28	3.01	<3.50	<0.21	2.48	<3.00	<0.50	116.0	457	434	625
1	D	NP	M	08/28	<2.00	<3.50	0.29	0.87	<3.00	<0.50	21.8	457	434	625
1	E	NP	K	08/28	5.13	<3.50	0.27	3.14	<3.00	<0.50	234.0	458	435	605
1	E	NP	L	08/28	4.53	<3.50	0.24	3.30	<3.00	<0.50	101.0	458	435	605
1	E	NP	M	08/28	<2.00	<3.50	<0.21	1.28	<3.00	<0.50	16.0	458	435	605
1	F	NP	W	08/28	4.25	<3.50	0.23	1.33	5.14	<0.50	113.0	344	331	290
1	AG	NP	W	08/28	32.80	<3.50	0.26	1.51	20.90	<0.50	125.0	357	346	300
20	A	LS	K	08/18	11.10	<3.50	0.46	6.02	<3.00	<0.50	55.1	342	368	400
20	A	LS	L	08/18	<2.00	<3.50	0.33	4.50	<3.00	1.08	110.0	342	368	400
20	A	LS	M	08/18	<2.00	<3.50	0.31	1.38	<3.00	<0.50	33.5	342	368	400
22	A	AG	W	08/19	20.20	<3.50	1.43	3.63	31.20	<0.50	92.7	338	310	330
22	B	AG	W	08/19	18.00	<3.50	1.23	4.26	25.80	<0.50	104.0	309	283	235
22	C	AG	W	08/19	35.00	<3.50	1.26	4.50	41.00	0.52	135.0	322	293	270
22	D	AG	L	08/19	7.25	3.57	3.00	22.70	<3.00	<0.50	182.0	367	339	440
22	D	AG	M	08/19	<2.00	<3.50	2.00	3.12	<3.00	<0.50	42.7	367	339	440
22	E	AG	W	08/19	17.80	<3.50	1.17	2.27	28.70	<0.50	112.0	335	302	315
22	A	NP	K	08/18	3.85	<3.50	0.22	4.43	<3.00	1.15	232.0	530	507	1025

Appendix J continued

Site	Rep.	S	T	Date	Mn	Ni	Pb	Se	Sr	V	Zn	T.L.	F.L.	WT
22	A	NP	L	08/18	2.55	<3.50	0.27	3.62	<3.00	<0.50	63.3	530	507	1025
22	A	NP	M	08/18	<2.00	<3.50	<0.21	1.45	<3.00	<0.50	16.6	530	507	1025
22	B	NP	L	08/19	5.06	<3.50	<0.21	4.31	<3.00	<0.50	105.0	416	395	490
22	B	NP	M	08/19	2.86	<3.50	<0.21	1.92	<3.00	<0.50	19.5	416	395	490
23	A	AG	W	08/23	7.47	<3.50	2.23	3.19	4.18	<0.50	108.0	307	285	240
23	A	LS	K	08/25	8.80	10.70	<0.21	2.34	<3.00	<0.50	200.0	325	346	292
23	A	LS	L	08/25	16.40	4.05	<0.21	3.02	<3.00	<0.50	76.1	325	346	292
23	A	LS	M	08/25	7.92	<3.50	<0.21	2.21	7.89	<0.50	30.0	325	346	292

[a] AG = Arctic Grayling, LS = Longnose Sucker, NP = Northern Pike.
[b] K = Kidney, L = Liver, M = Muscle; [c] T.L. = Total Length, F.L. = Fork Length, WT. = Weight.

APPENDIX K: FISH AND MAMMAL TISSUE, 1989 (RAW DATA)

Metals concentrations of muscle and whole body, and total length (mm), fork length (mm) and weight (gm) of lake chub (*Coueseius plumbeus*), and northern pike (*Esox lucius*), and metals concentrations of marten (*Martes americana*), and mink (*Mustela vison*) collected from Kanuti National Wildlife Refuge, Alaska, 1989.

					Metals Concentrations (mg/kg dry weight)										
Site	Rep.	Species	Matrix	Date	Al	Ba	Cu	Fe	Hg	Mg	Mn	Sr	T.L.	F.L.	Wt.
1	A	NP[a]	Muscle	07/05	<3	<0.20	0.77	6	0.24	1480	2.0	1.4	275	260	140
1	B	NP	Muscle	07/05	<3	0.20	0.40	5	0.80	1390	1.0	1.1	228	215	75
2	B	NP	Muscle	07/08	<3	0.10	0.50	1	0.71	1370	2.0	2.0	500	438	414
2	A	NP	Muscle	07/08	<3	0.10	0.30	1	0.60	1410	1.0	1.4	617	592	1425
3	A	NP	Muscle	07/06	<3	<0.20	0.30	1	1.70	1390	2.0	1.2	700	667	1950
3	B	NP	Muscle	07/07	<3	<0.20	0.30	1	2.90	1390	2.0	1.2	843	836	4900
3	C	NP	Muscle	07/07	<3	0.40	0.50	6	1.80	1410	3.1	1.6	534	520	910
3	D	NP	Muscle	07/07	<3	0.30	0.30	<1	1.04	1440	3.9	1.6	457	431	625
3	E	NP	Muscle	07/07	7	0.46	0.30	6	1.50	1450	11.0	1.6	465	440	600
4	A	NP	Muscle	07/08	<3	0.40	0.40	<1	2.90	1330	1.0	1.7	636	605	1650
4	A	CH	WB[b]	07/08	425	6.50	5.60	446	0.31	1560	27.0	54.7	134	120	20
5	A	NP	Muscle	07/06	<3	0.30	0.40	16	3.20	1320	4.0	1.1	740	710	2850
5	B	NP	Muscle	07/06	<3	0.54	0.60	5	1.40	1440	3.7	1.6	523	490	675
6	A	NP	Muscle	07/06	<3	0.56	0.69	4	0.56	1390	3.8	2.6	326	308	200
6	B	NP	Muscle	07/06	5	0.40	0.60	6	1.90	1380	2.0	1.1	490	473	775
15	A	NP	Muscle	07/14	14	1.40	0.50	16	0.31	1480	4.7	6.2		313	
15	B	NP	Muscle	07/14	21	0.77	0.50	22	0.56	1350	4.0	3.3	456	427	500

Appendix K Continued

Site	Rep.	Species	Matrix	Date	Al	Ba	Cu	Fe	Hg	Mg	Mn	Sr	T.L.	F.L	Wt.
15	C	NP	Muscle	07/14	3	0.40	0.30	4	2.30	1390	2.0	2.0	707	657	1825
17	A	NP	Muscle	7/14	17	0.43	0.40	21	0.34	1390	2.0	2.0	508	482	725
19	A	SS	WB	07/14	150	8.40	2.90	232	2.00	1530	68.0	58.5			20 total
20	A	SS	WB	07/05	750	13.00	4.40	896	0.14	1810	75.0	67.4		mean 62	4 total
22	A	NP	Muscle	07/05	<3	<0.20	0.30	<1	0.79	1370	<1.0	1.0		645	
43	A	NP	Muscle	07/14	20	1.00	0.90	10	0.35	1330	4.9	4.4	503	478	725
43	B	NP	Muscle	07/14	9	0.98	0.30	16	1.80	1460	4.2	3.4	443	417	525
43	C	NP	Muscle	07/14	7	1.00	0.30	12	0.48	1430	7.2	6.8	522	495	775
43	D	NP	Muscle	07/14	5	0.47	0.30	8	0.48	1350	2.0	3.3	502	475	725
44	C	Ma	Muscle	1989	8	0.20	13.00	239	0.09	931	1.0	<0.2			
44	B	Ma	Muscle	1989	3	0.30	10.00	198	0.31	820	1.0	0.5			
44	A	Mi	Muscle	1989	<3	0.40	8.30	274	0.32	666	1.0	0.4			

[a] LC = Lake Chub, NP = Northern Pike, SS = Slimy Sculpin, Ma = Marten, Mi = Mink.

[b] WB = Whole Body.

APPENDIX L: MARTEN HAIR, 1989 (RAW DATA)

Metals concentrations (mg/kg dry weight) of marten hair collected near Site 10 during 11/89 and 12/89 from Kanuti National Wildlife Refuge, Alaska, 1989. Actual sample sites were west and southwest of Site 10.

Ag	Al	B	Ba	Be	Cd	Co	Cr	Cu	Fe	Hg	Mg	Mn	Mo	Ni	Pb	Sb	Sr	Sn	V	Zn
<4.5	16	2.8	<1.5	<0.3	<0.3	<1.5	2.4	7.55	55	<0.1	90	9.58	<1.5	<1.5	1.38	<1.1	<1.5	<12	<1.5	171
<4.5	61	<1.5	<1.5	<0.3	<0.3	<1.5	<1.5	6.19	136	0.41	85	5.72	<1.5	<1.5	0.57	<0.4	<1.5	<12	<1.5	112
<4.5	21	21.0	<1.5	<0.3	<0.3	<1.5	<1.5	9.31	115	0.71	104	7.28	<1.5	<1.5	1.70	<0.6	<1.5	<12	<1.5	157

APPENDIX M: WOLF HAIR, 1990 (RAW DATA)

Mercury concentrations (mg/kg-dry weight) of 14 wolf hair samples collected from Kanuti National Wildlife Refuge, Alaska, 1990.

Hg
0.2510
0.3350
0.2230
0.1330
0.3010
0.2730
0.2900
0.1800
2.8800
0.2020
0.3840
0.3150
0.1430
1.4000

APPENDIX N: LITERATURE CITED FOR APPENDICES

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