

TECHNICAL REPORT

CONTAMINANT DATA FOR WATER, SEDIMENTS, AND FISH  
OF KOYUKUK NATIONAL WILDLIFE REFUGE AND THE NORTHERN UNIT  
OF INNOKO NATIONAL WILDLIFE REFUGE

by

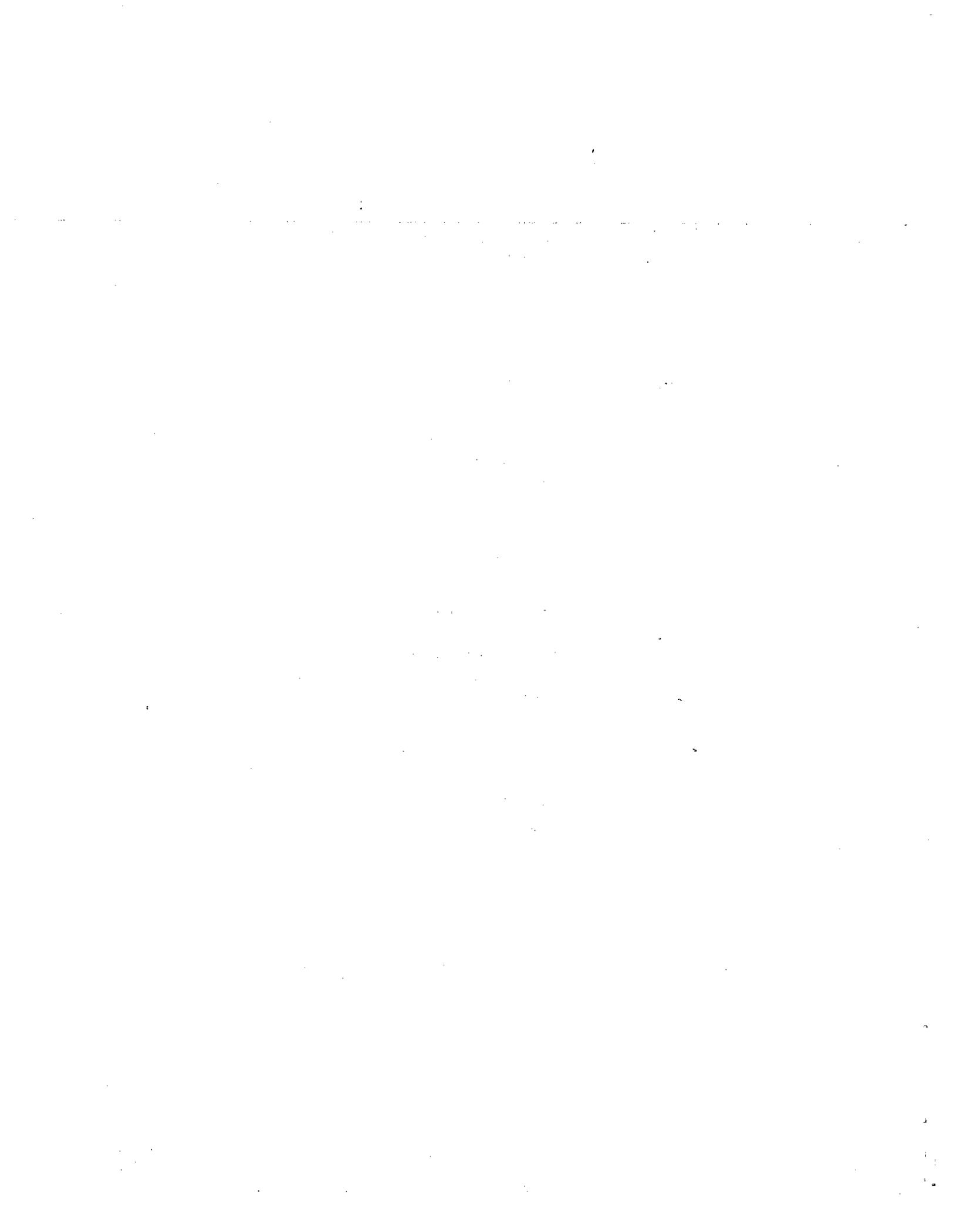
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## Preface

The Koyukuk National Wildlife Refuge and the Northern Unit of the Innoko National Wildlife Refuge were established under the Alaska National Interest Lands Conservation Act of 1980 to protect water quality, fish and wildlife populations, and subsistence use of refuge lands, as well as to fulfill international treaty obligations with respect to fish and wildlife. This study was initiated to examine possible impacts of mining on these refuge resources, including water, sediments, and fish, and to determine baseline trace element concentrations in these matrices in different refuge rivers. Placer and hard rock mining have been significant elements in the development of Alaska's mineral resources and economy. Many early practices, including mining within active stream beds without stream diversions, settling ponds, or water recycling; haphazard use and disposal of mercury used to form a gold amalgam; and mine development without restoration, have had profound impacts on Alaska's lands, waters, fish and wildlife. Some of these practices have undoubtedly left a contaminants legacy.

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

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



## Executive Summary

Studies were conducted by the U.S. Fish and Wildlife Service (USFWS) between 1986 and 1988 to obtain trace element and water quality data on water, sediments, and fish in rivers of the Koyukuk and Innoko Refuges and to assess the impacts of upstream placer and hard rock mining activities. This report only addresses data obtained in the Koyukuk National Wildlife Refuge and the Northern Unit of the Innoko National Wildlife Refuge, currently under management by Koyukuk National Wildlife Refuge staff. Data from the southern portion of the Innoko National Wildlife Refuge has been previously reported (Jackson 1990).

None of the sampling in these studies occurred during active mining, and all study sites had experienced some mining in the drainages. Therefore, proper reference sites were lacking in this study. Nevertheless, valuable baseline water quality and contaminants data were obtained for performing before/after comparisons should mining resume on the drainages sampled.

Study sites resembled many other nonglacial interior Alaska streams and rivers -- slightly acid to moderately basic in pH, soft to moderate in hardness, and low to average in alkalinity. Waters are typical of calcium-magnesium bicarbonate watersheds. All sites except the Hogatza River and the Koyukuk River had low turbidities for rivers. Measurable settleable solids were observed in the Koyukuk River and in Caribou Creek, and comparatively high suspended solids were measured in the Hogatza River, Koyukuk River, and Caribou Creek in 1987. Caribou Creek's turbidity was only slightly elevated and Clear Creek was very low in turbidity, indicating that the source of turbidity on the Hogatza River was being derived from other sources at the time of sampling, and not directly from these formerly mined streams. The comparatively high turbidity, settleable solids, and suspended of these rivers in 1987 was not observed in 1988, suggesting that the higher turbidity may occur episodically, following flood events.

With a few notable exceptions, surface waters examined in this study were relatively uncontaminated by metals. Vanadium concentrations in refuge surface waters were observed only in 1986 in single grab samples and appear elevated ( $> 0.01$  mg/L) at the Hogatza River, Bishop Creek, and the Gisasa River. High aluminum concentrations were found in the Hogatza River, as well as in two tributaries to the Hogatza River, Caribou Creek and Clear Creek. In combination with the low alkalinities observed in this watershed, the aluminum could pose a toxicity threat to sensitive species, particularly under lower pH ( $< 6.5$ ) conditions. Other metals elevated in water are iron, manganese, copper, and nickel. Iron concentrations were elevated on the Hogatza, Koyukuk, Huslia, and Dulbi rivers, and as well as Bishop and Bonanza creeks; concentrations often approached or violated the State drinking water quality standard during one or more sample periods. Manganese concentrations also exceeded the State criterion on the Hogatza River in 1987. Copper concentrations in water were slightly elevated in the Hogatza, Dulbi, and Gisasa rivers in 1986, the Hogatza and Koyukuk rivers in 1987, and the Hogatza, Koyukuk, and Bonanza drainages in 1988. These conditions are not

unusual for interior or northern Alaska drainages and are probably natural. Nickel concentrations in water at a number of refuge sites also appear to be slightly higher than those usually reported for unpolluted freshwater, but not sufficiently high to result in adverse effects.

Sediment samples were only collected in 1987 and 1988. Koyukuk River and Bonanza Creek sediments contained significantly more copper and nickel than observed in Clear Creek sediment, which contained the lowest concentrations of these metals. The concentrations of arsenic, copper, and nickel in sediments at these sites were also enriched compared to most unpolluted freshwater sediment. Högatza River and Bonanza Creek sediments contained more iron than other sites, especially Clear Creek, with the lowest iron concentrations. Since all drainages have been influenced by mining, at least historically, it is not possible to discriminate between differences attributable to mining and natural among-site variability until additional unmined reference sites in each area are studied.

Sufficient northern pike were obtained for trace element analysis and statistical treatment from all study sites except Clear Creek, where only Arctic grayling were obtained. Generally, concentrations of trace elements in pike and grayling muscle appear normal in relation to fish elsewhere and no among-site differences were consistently demonstrated in metal content of fish muscle samples in the 1987 data set. In 1988, significant among-site differences were observed in the concentrations of barium, copper, iron, manganese, strontium, and zinc in fish muscle samples. Three unusually high copper concentrations were observed in northern pike muscle samples collected in 1988, including two fish from Bonanza Creek and one fish from Caribou Creek, but the significance of these levels in tissues is unknown. Similarly, one unusually high nickel concentration and two relatively high zinc concentrations were observed in fish tissues in the 1988 data set.

Metal concentrations in fish livers were also generally within expected ranges. Barium, cadmium, chromium, molybdenum, and vanadium were present in some fish livers, while copper, iron, magnesium, manganese, selenium, tin and zinc were present in all fish livers. The only among-site differences observed in metal concentrations in pike livers were for iron and zinc. One unusual finding was the occurrence of silver in one pike liver from Bishop Creek. Boron was rarely detected in northern pike livers, but was observed in all three grayling analyzed from Clear Creek, although not in high enough concentrations to induce toxicity.

Fish kidneys were only analyzed in 1987. Antimony, rarely detected in muscle or liver tissue, was detected in all the pike kidneys analyzed from the Koyukuk River, Bishop Creek, and Bonanza Creek. The highest cadmium concentration observed, 8.00 mg/kg in a northern pike from Bonanza Creek, if correct, is anomalously high. Silver was detected in the kidney from the same Bishop Creek pike with silver in its liver. Other metals were present in concentrations that appear within the normal range.

The relationship between fish growth and site was also investigated. No significant differences in northern pike length, weight, or condition index occurred among sites. Also, correlations between northern pike length, weight, and condition index and trace element concentrations, when observed, appeared weak and unlikely to strongly influence fish growth or condition.

One unfortunate casualty of our quality control/quality assurance screening was mercury in all three media -- water, sediments, and fish tissues. Nevertheless, it is important to point out that, according to analytical results, mercury was present in fish muscle tissue, as well as other tissues, sometimes at concentrations probably equally to or greater than 1 mg/kg wet weight. Concern therefore remains that certain watersheds on these refuges contain mercury-contaminated fish that present a possible health hazard to fish, wildlife, and subsistence users, particularly if use of northern pike is frequent in areas where mercury concentrations are high. Until quality data are obtained for mercury and source areas of mercury are better defined, the amount of risk from mercury in fish from these watersheds remains uncertain.



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## Introduction

### *History and Purposes of the Refuges*

The Koyukuk National Wildlife Refuge (Refuge) and the Northern Unit of the Innoko Refuge, created by the Alaska National Interest Lands Conservation Act of 1980 (ANILCA), are located in west central Alaska. Purposes of the Koyukuk Refuge, prescribed in Section 302(5)(B) of ANILCA, include:

- (1) conservation of fish and wildlife populations and habitats in their natural diversity, including ... waterfowl and other migratory birds, moose, caribou, ... furbearers, and salmon;
- (2) fulfillment of international treaty obligations concerning fish, wildlife, and their habitats;
- (3) provision of the opportunity for continued subsistence uses by local residents consistent with other purposes of the refuge; and
- (4) ensuring water quality and quantity, to the maximum extent practicable, within the refuge.

Major purposes for which the Northern Unit of the Innoko Refuge was established, set forth in Section 302(3) of ANILCA are the same as for Koyukuk Refuge except for the first purpose:

- (1) conservation of fish and wildlife populations and habitats in their natural diversity, including ... waterfowl, peregrine falcons, other migratory birds, black bear, moose, furbearers, and other mammals and salmon.

### *Refuge Resources*

#### Habitats

More than 8800 km (5500 mi) of rivers and streams, with numerous side sloughs, an estimated 73,800 ponds and lakes, and nearly 3 million acres (4100 mi<sup>2</sup>) of wetlands are found in the refuges. The 3.6-million-acre Koyukuk Refuge consists of extensive lowlands situated in the circular floodplain basin of the Koyukuk River and drained by the Yukon River to the south. It is bounded on the west by the Nulato Hills, on the north by the Purcell Mountains and Zane Hills, and on the east by the Galena Mountains. The northwestern corner of this refuge abuts Selawik Refuge. The Koyukuk River and surrounding Koyukuk Flats, from 8 to 32 km (5-20 mi) wide, are major features of the Koyukuk refuge, with the river bisecting the entire refuge into southeastern and northwestern sections. Approximately

483 km (300 mi) of the 1100-km (684-mi) Koyukuk River fall within Koyukuk Refuge boundaries.

The 351,000-acre Northern Unit of Innoko Refuge, also known as the Kaiyuh Flats, lies southwest of Koyukuk Refuge and also encompasses extensive wetlands in the floodplains of the Kaiyuh and Yukon rivers. The Yukon River forms the northern and western boundary of this unit, and the Kaiyuh Mountains form the southern boundary.

## Fish and Wildlife

The wetland habitats of the refuge are highly productive for waterfowl, producing approximately 265,000 ducks and 8,000 geese in 1983 (King and Conant 1983, USFWS 1987). However, from 1987 to 1992, lower numbers, about 100,000 ducks and 3000 geese were produced (Koyukuk Refuge, unpublished data). The most common duck species are green-winged teal (*Anas crecca*), American wigeon (*A. americana*), mallards (*A. platyrhynchos*), northern shovelers (*A. clypeata*), northern pintail (*A. acuta*), and greater and lesser scaup (*Aythya marila* and *A. affinis*). Greater and lesser yellowlegs (*Tringa melanoleuca* and *T. flavipes*) and many other shorebirds are also common on the refuges. King and Conant (1983) also estimated that an average of 700 sandhill cranes (*Grus canadensis*) bred annually in the Koyukuk Flats area from 1974 to 1983. Other important nesting migratory birds include tundra and trumpeter swans (*Cygnus columbianus* and *C. buccinator*), whose ranges overlap on the refuges; greater white-fronted geese (*Anser albifrons*); and lesser Canada geese (*Branta canadensis taverneri*).

At least three pairs of the endangered peregrine falcon (*Falco peregrinus*) have also been reported nesting along the Koyukuk River in Koyukuk Refuge, and at least 21 pairs nest along the north bank of the Yukon River adjacent to the Northern Unit of Innoko Refuge (Peter Bente, U.S. Fish and Wildlife Service, Fairbanks, pers. comm.).

The frequent fire cycles and flooding of the Koyukuk River, its major tributaries (the Gisasa, Kateel, Huslia, and Dulbi river systems), and other drainages of the refuges, together with abundant wetlands and forested floodplains offer prime habitat for significant populations of fish, furbearers, moose (*Alces alces*), black bears (*Ursus americanus*), and gray wolves (*Canis lupus*).

Twenty-one fish species have been reported on the refuges (USFWS 1992). Among the abundant fish within refuge rivers are chum salmon (*Oncorhynchus keta*), with major summer spawning and migration runs in the Koyukuk, Dakli, Gisasa, Indian, Kateel, and Huslia rivers and Billy Hawk Creek. Other common species are coho and chinook salmon (*O. kisutch* and *O. tshawytscha*), Arctic grayling (*Thymallus arcticus*), broad and humpback whitefish (*Coregonus nasus* and *C. pidschian*), round whitefish (*Prosopium cylindraceum*), Bering and least cisco (*C. laurettae* and *C. sardinella*), sheefish (*Stenodus leucichthys*), lake chub (*Couesius plumbeus*), longnose sucker (*Catostomus catostomus*), burbot (*Lota lota*), and

northern pike (*Esox lucius*) (Morrow 1980, Alt 1984). Chum and chinook salmon from the Koyukuk and the Northern Unit of the Innoko Refuges represent important stocks of salmon in commercial Yukon River fisheries, and are also fished on the high seas (USFWS 1992). Chum salmon and whitefish from the Yukon River and the Koyukuk River, primarily near Huslia and Hughes, are also main components of the subsistence fishery near the refuges (USFWS 1992). Trophy-sized northern pike, within the Kaiyuh Flats, and Arctic grayling, within stream headwaters, are important sport fish, particularly during the fall hunting season.

## Geology, Mineral Occurrences, and Mining History

*Geology.* Both Koyukuk Refuge and the Northern Unit of Innoko Refuge are within the Yukon-Koyukuk Basin, a huge (approximately 250,000 km<sup>2</sup>) depression that stretches across western Alaska from the Brooks Range on the north to the Yukon Delta on the south (Nilsen 1989, Patton and Box 1989). The Melozitna and Yukon rivers appear to form the hypotenuse on the southeastern side (Cass 1959, Berg and Cobb 1967), but the southwesternmost extent of the basin, which extends under the Yukon Delta and into the Bering Sea has not yet been delineated. The refuges occupy the Koyukuk Flats, one of five lowlands with elevations generally between sea level and 200 meters high (Cady 1989).

The geologically complex, broadly triangular Yukon-Koyukuk Basin, consisting of predominately Cretaceous-aged sedimentary and volcanic rocks, has an enigmatic history. The basin itself is underlain by accreted oceanic volcanic and volcanoclastic material assumed to have been part of an island arc - trench system and/or an underwater sea mount system (Patton and Box 1989). Two main subbasins, the Kobuk-Koyukuk and Lower Yukon subbasins, are separated by a remnant volcanic arc (Koyukuk terrane). Flanking the basin are mountainous terranes of much older (Proterzoic and Paleozoic) origin, consisting of continental sedimentary rocks metamorphosed in the late Mesozoic (the Seward terrane on the west, the Arctic Alaska terrane [Brooks Range] on the north, and the Ruby terranes on the east). Between the basins and these borderlands is a narrow, highly tectonized horseshoe-shaped belt opening to the southwest, consisting of oceanic crust and mantle rock outcrops that dip basinward (Angayucham-Tozitna terrane).

Geologic, topographic, gravity, and aeromagnetic data on the region suggests a history of collision and partial underthrusting of a passive continental margin beneath a colliding volcanic island arc in early Cretaceous time (Cady 1989, Patton and Box 1989). The three borderland terranes, although similar in composition (dominated by pelitic schist, quartzite and carbonate rocks), are suspected of arriving in their present positions as separate allochthonous terranes, since segments cannot be traced into one another (Patton and Box 1989). Uplift and erosion throughout the Cretaceous period resulted in large volumes of terrigenous sediments being rapidly deposited in the deep basins. Subsequent large-scale counterclockwise rotation of the northern continental borderland occurred, resulting in an offset of the two subbasins.

Except for the mountains to the north and west of the Koyukuk Refuge, the area is overlain by thick layers of Tertiary and Quaternary sediments, including basalt and colluvial, alluvial, fluvial, eolian, lacustrine, shoreline, and shallow marine deposits, which obscure lode mineral occurrences (Nilsen 1989). Active dunes occur along the western border and the northern borders of the Koyukuk Refuge and areas along the northern border are mantled with glacial till from local glaciation in the Purcell Mountains and Zane Hills. The sedimentary fill is as thick as 3000 - 3500 m in the Lower Yukon Basin. However, in the Koyukuk Flats region, sediments are much thinner, ranging from several meters to several hundred meters in thickness owing to a broad arching of the crust. Thick deltaic deposits, including quartzose sandstone, shale, and thin seams of bituminous coal, extend westward in a broad belt along the southeast side of the basin from 66°N to the lower Yukon River.

Plutonism began in the Upper Jurassic(?) to Lower Cretaceous in the west end of the basin and progressed eastward. This intrusive activity, accompanied by volcanism through the mid-Cretaceous period, produced rugged volcanic-plutonic complexes following an east-to-west trend north of Koyukuk Refuge (Patton and Box 1989). The granitic rock mountains in this region include the Selawik Hills, Purcell Mountains, Zane Hills, and Indian Mountain. This belt continues to the southwest through the Seward Peninsula to St. Lawrence Island and then northwestward into the Chukotsh Peninsula of Siberia, and is also believed to extend to the Canadian border (Liss, pers. comm.). Miller (1989) recognized two plutonic suites within the belt that overlap geographically. A volumetrically large series of plutons extends to the west, arcing between the Purcell Mountains in the east to Granite Mountain in the west and on to eastern Siberia. An alkaline pluton series forms a smaller, but extensive sinuous belt from near the Zane Hills to Cape Dezhnev in eastern Siberia. This latter series, including the Hogatza plutonic belt, is recognized as forming a distinct metalliferous province. Gold from the area is derived from volcanic-plutonic complexes and rhyolite sills, intruding thick and extensive Mesozoic sedimentary deposits (Bundtzen et al. 1987).

*Mineral Deposits in the Refuges and Surrounding Areas.* Sites of known or indicated mineralization in and near the refuges (Eberlein et al. 1977; Cobb 1970, 1972, 1974, 1975a,b, 1984a,b,c,d,e, 1985; Cobb and Chapman 1981; Cruz and Cobb 1984a,b, 1986; U.S. Bureau of Mines 1987; Alaska Division of Geological and Geophysical Surveys 1991) are identified in Figure 1. Gold, in lode sources and in placers, has been the dominant mineral since mining began in all quadrangles surrounding the refuges. However, very few stream placer or minable metal deposits have been located within the refuges. One mineralized area occurs south of Indian River, near the northern boundary. This area is enriched in bismuth, chromium, copper, manganese, molybdenum, thorium, uranium and zinc (Cobb 1972; Alaska Division of Geological and Geophysical Surveys 1991). Sun Mountain also has at least two sites with minor shows of lead, copper, and silver (Miller and Ferrians 1968, USFWS 1987).

Although mercury occurs in altered zones of metamorphic rock on the Seward Peninsula to the northwest (Nelson et al. 1975), no mercury deposits have been documented within the five quadrangles represented by the refuges, Shungnak, Hughes, Kateel River, Melozitna, and

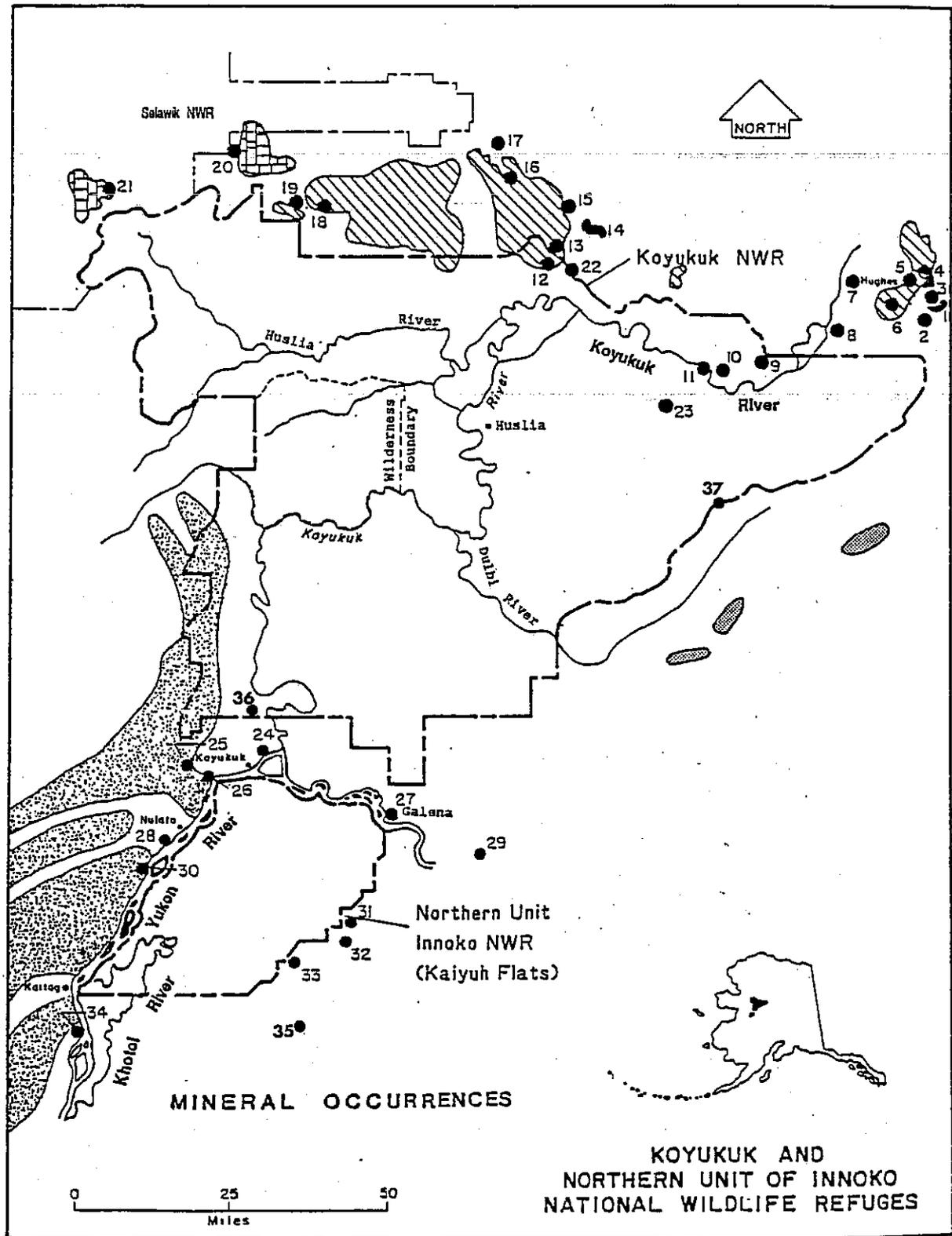


Figure 1. Regional mineral occurrences near Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge.

## Legend - Mineral Occurrences

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

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

Terranes favorable or permissible for mineral deposits



Alkalic granite



Undivided granite, including alkalic plutons - Au



Ophiolite terrane - Cr, Co, Ni, Pt



Coal-bearing sandstone and shale

Nulato (Bottge 1986). However, hot spring mercury was noted in the region of the Galena mine adjacent to the Northern Unit of the Innoko Refuge (Nokleberg et al. 1987) and placers in the Yukon River region sometimes show cinnabar (HgS) in the gravels (Malone 1962).

Most mineral resources of the region are concentrated north of the Koyukuk Refuge in the heavily mineralized Hogatza plutonic belt in the Indian Mountain - Purcell Mountain - Zane Hills region, with gold-lead-silver as primary metals and molybdenum-copper-uranium as secondary metals (Clark et al. 1974). In addition to five sites with placer gold deposits (Cobb 1984a), five lode deposits of gold (Cobb 1974, 1984b) occur in this region. Bear Creek, draining Caribou Mountain in the Zane Hills, a tributary to the Hogatza River and approximately 56 km (35 mi) north of the refuge, is the site of extensive placer gold deposits (Cobb 1984a). Other elements present in this region in potentially minable amounts include copper (Cobb 1984c), zinc (Cobb 1975a), antimony (Cruz and Cobb 1986), lead (Cobb 1984d), molybdenum (Berg and Cobb 1967, Cobb 1984e), and platinum-group metals (Cobb 1975b). The Purcell Mountains show potential for lead, as well as many of the above metals, especially copper, uranium, thorium, and silver. The region is also enriched in barium, chromium, nickel, tungsten, silver, arsenic, and, in a few locations, iron (Liss, pers. comm.). The Purcell Mountains are also rich in lead, as well as many of the above minerals, especially copper, uranium, thorium, and silver (Liss, pers. comm.). In the Upper Billy Hawk Creek area, a 26-km<sup>2</sup> (10-mi<sup>2</sup>) area contains one- to two-foot thick quartz veins with visible silver, lead, and copper.

Radioactive veins are known to be present in the vicinity (Cobb 1970, Barker 1985), suggesting the potential of minable deposits. Uranium, thorium, lanthanum, and other rare earths occur in concentrations as high as 200 times background concentrations elsewhere (Barker 1985; Shirley Liss, Alaska Division of Geological and Geophysical Surveys, Fairbanks, pers. comm.). Parts of the region are also enriched in barium, chromium, nickel, tungsten, silver, arsenic, and, in a few locations, iron (Liss, pers. comm.).

The Northern Unit of Innoko Refuge is bordered on the east by the Kaiyuh Mountains, which are part of a metal province characterized by tin-tungsten-gold-lead-zinc metals with secondary sources of copper-antimony-silver (Clark et al. 1974). Lead, as the mineral galena (PbS), occurs in the region (Holzheimer 1926). The region also contains polymetallic veins in basalts with copper, gold, and antimony as the primary metals (Nokleberg et al. 1987).

Across the Yukon River, west of the Northern Unit of Innoko Refuge, lies the Nulato coal field. This unit, with bituminous and subbituminous coal seams to one meter thick with occasionally deeper pockets, extends from south of the Kateel River's confluence with the Yukon River to the southwestern boundary of the Northern Unit (Chapman 1963; Patton 1966). Oil and gas potential in the region is low.

*Mining History of the Refuge Areas.* Historic mining activity in the area of the Koyukuk Refuge and Northern Unit of Innoko Refuge is summarized in Figure 2. Data are based on data from Miller and Ferrians (1968), Eberlein et al. (1977), U.S. Bureau of Mines Mineral Industry Locator System records, U.S. Bureau of Mines (1987), and USFWS (1987). Gold has been the primary metal mined in the Koyukuk district, with 8.6 million grams (278,000 troy ounces) recovered since discovery of gold in the area in 1898 until 1959 (Baggs et al. 1988). Much of this gold was mined from placers north of the refuge in the Hughes - Indian River - Zane Hills area. Gold was first discovered in this region by Roy Hughes in 1901 at Hughes Bar, a beach site two miles north of the present village of Hughes on the Koyukuk River. Mines were then established on Indian River and its tributaries around 1910. These mines were mostly abandoned by about 1915, but some additional mining occurred in the vicinity until 1965. Gold mining also occurred on Utopia Creek from 1930 to 1962.

Three placer mines occurred on the tributaries to the Hogatza River draining the Zane Mountains. These include the Bear Creek, Dry Creek, and Clear Creek mines. The mine on Bear Creek, which drains into Caribou Creek approximately 5 km (3 miles) from its entry into the Hogatza River, has been the most highly productive of the mines in this region. Gold was discovered at this site in 1937 and a mining camp was established at the site about 1940. Active mining was renewed in 1955 using bulldozers and front-end loaders, as well as an 8-ft<sup>3</sup> bucketline dredge by the Alaska Gold Company (Buntzen et al. 1985). From 1957 to 1975, the mine was worked by dredge, with total production exceeding 6.2 million grams (200,000 troy ounces). The mine was again in operation from 1981 to 1984 and from 1990-1991 (Liss, pers. comm.). Dry Creek mine, on a tributary to Bear Creek, has been intermittently mined by U.S.S.R. & M. since 1958. Placer gold was also mined from Clear Creek, just to the north of Caribou Creek, from 1934 to 1936. The mine was reactivated in 1968 by Alaska Gold Company and has been intermittently active since then.

Only one documented active mining claim occurs within the Koyukuk Refuge boundaries. This claim is located along the Indian River near the northern boundary. Production from this claim has not been confirmed.

Approximately 15 lode claims have been filed on the eastern border of the Northern Unit of Innoko Refuge on Bishop Creek. Lead-silver ore was first produced from Bishop Creek early in this century. The town of Galena was established in 1919 as a supply point for the ore. The principal producing mine was the Galena Mine (Holzheimer 1926), also known as the Perseverance Mine (Nokleberg et al. 1987). Approximately 231 metric tons of ore, consisting of 73 percent lead, and 124 g/ton silver, were removed from subsurface veins between 1920 and 1927. The mine was reopened in 1981. Silver was also mined from the headwaters of Bishop Creek. One active gold lode mine claim has been active since 1979. South of this area within the Northern Unit of Innoko Refuge, placer gold was also mined from Camp Creek in the early 1980's, and this claim is still active. Further south of the refuge unit, chromite, copper, silver and gold prospects also occur.

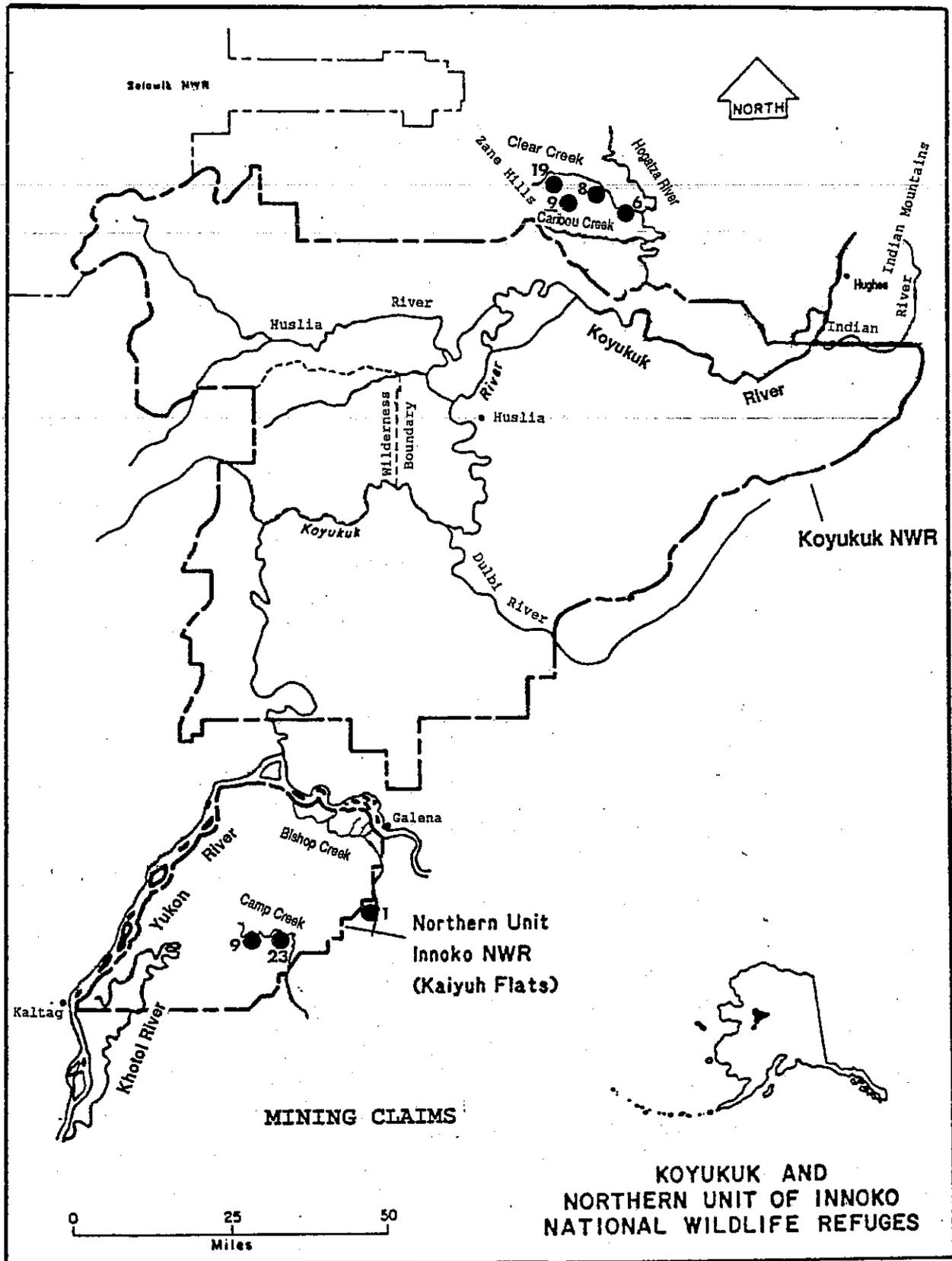


Figure 2. Regional mining claims near Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge.

## **Legend - Mining Claim Activity**

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### **Recent Mining Claims near the Koyokuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge**

#### **Hogatza River Area (Hughes Quadrangle)**

6. T9N, R15E, Sections 15-17  
Four Au placer claims  
Alaska Gold Co. 1986-1991
8. T9N, R14 and 15E, Sections 1-3, 6-8, 11, 12  
24 Au placer claims  
Alaska Gold Co. 1977-1991
9. T9N, R14 and 15E  
2 Au placer claims (patented)  
U.S.S.R. & M. Co. 1944 only
19. T9N, R15E, Sections 5 and 6  
T9N, R14E, Section 34  
T10N, R14E, Sections 25, 26, 34-36  
T10N R15E, Sections 27 and 28  
26 Au placer claims  
Alaska Gold Co. 1985-1991

#### **Camp and Bishop Creeks Area (Nulato Quadrangle)**

1. T12S, R8E, Sections 23-36  
15 Ag, Pb lode claims  
Joe Manga 1979-1991
9. T13S, R7E, Sections 4, 5, 7, 8, 17, 18, 20  
17 Au placer claims  
Jasper Heath 1974-1986
23. T13S, R7E, Sections 5, 8  
48 Au placer claims  
Carl Bracale 1984-1991

Coal has also been mined from exposed seams along the Yukon River, including the Pickert, Busch, Nahoclatilten and Blatchfort bituminous coal mines on the western border of the Northern Unit of Innoko Refuge. Most of the coal was mined from 1898 to 1902 for use by steamships traveling on the Yukon River. Only small-scale, local use of coal resources is presently anticipated due to the irregularity and size of the seams.

Placer and lode exploration for gold, other precious minerals, and base minerals have increased dramatically in Alaska in the eighties compared to previous years and continue to grow (Alaska Department of Natural Resources 1982; Swainbank et al. 1990; U.S. Dept. Interior 1990). Deregulated gold prices, removal of ownership restraints in the early 1970's, increased instability in the world economy, and new technologies for mineral detection and recovery suggest the potential for increased mining activities near and on interior Alaskan refuges (Anonymous 1980; Swainback et al. 1990; U.S. Dept. Interior 1990).and 1927.

### *Study Objectives*

To meet refuge goals, Section 304(g)(2G) mandates identification and description of problems which may adversely affect fishery resources and wildlife populations. The USFWS (1987) identified agricultural or recreational development, placer mining within and near refuge boundaries, timber harvesting, and development of transportation corridors as potentially affecting water quality, fish and wildlife populations, and their habitats. Preliminary sampling of metal concentrations in water was conducted in 1986 by refuge personnel. Study objectives were subsequently described and expanded in 1987 and 1988. Objectives were:

1. To monitor water quality and contaminant concentrations of trace elements in water, stream sediments, and fish from the Koyukuk and Northern Unit of Innoko Refuges including the Hogatza, and Koyukuk rivers and Bishop, Clear, Caribou, and Camp creeks and to obtain preliminary trace element data on water from the Huslia, Kateel, Dulbi, and Gisasa rivers.
2. To evaluate existing and potential impacts of metal contamination and water quality degradation on refuge fish and wildlife populations.
3. To develop recommendations for future monitoring to protect water quality, conserve fish and wildlife populations, and to protect subsistence use, consistent with refuge purposes.

A survey of water quality and contaminant residue levels in water was initiated in 1984 by USFWS Fishery Resource personnel at several interior Alaska refuge sites (Deschermeier and Hawkinson 1985). This study included data on water quality and metal concentrations on the Hogatza River in June and September 1984. In 1986, ten water samples were collected from ten different sites on Koyukuk Refuge and the Northern Unit of Innoko Refuge for trace element analysis. Studies were continued by refuge personnel in coordination with a

contaminant specialist at six sites in 1987, when replicate sampling for total metals and dissolved metals in water, sediments and fish was performed. In 1988, this study was repeated. The 1986 - 1988 studies are described in detail in this report, and compared with 1984 data from the earlier study.

### *Study Rationale*

Gold deposits are often associated with other trace elements which may also be released to aquatic ecosystems during mining. In interior Alaska, arsenic, copper, zinc, and lead may be affiliated with gold, resulting in elevated concentrations of these metals in mined streams (Madison 1981; LaPerriere et al. 1985). Other metals sometimes found with placer and hard-rock deposits are antimony, aluminum, cadmium, chromium, iron, and mercury. Potential sources of mercury include mercury used historically to amalgamate gold; natural lodes of cinnabar (HgS); trace amounts of mercury in silty sediments of oceanic origin; volcanic or other thermally active zones; and global atmospheric deposition (Malone 1962; Wershaw 1970; Nelson et al. 1977; King et al. 1983; Wren and McCrimmon 1983; Barr 1986; Slemr and Langer 1992).

To extract the gold in ancient alluvia, large amounts of overburden are typically removed. Mined sediment-rich effluent, transported in suspension and as bedload, may cause elevated turbidities in the water column and blanket the stream bottom, making it unsuitable for aquatic life (Bjerklie and LaPerriere 1985; LaPerriere et al. 1985; Peterson et al. 1985; Wagener and LaPerriere 1985; Weber and Post 1985; Van Nieuwenhuysse and LaPerriere 1986; Lloyd 1987; Lloyd et al. 1987; Scannell 1988). Since 1985, Environmental Protection Agency (EPA) requirements for zero discharge of water and 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).

The abundance and productivity of plants, invertebrates, and fish can decline in streams with placer mines (Cordone and Kelley 1961; Van Nieuwenhuysse and LaPerriere 1986; Lloyd et al. 1987). Arctic grayling from mined streams may exhibit higher metal concentrations and liver and cellular abnormalities compared to fish from control streams (West 1982; West and Deschu 1984). Young grayling may also experience higher mean plasma glucose, depressed leucocrit levels, impaired feeding activity, reduced growth rates, and decreased survival in sediment-rich mined streams (McLeay et al. 1983, 1987; Reynolds et al. 1989). In water from mined streams, copper may occur at concentrations which are acutely toxic to invertebrates and early life stages of fish (EPA 1980a). Alaskan Arctic grayling are especially sensitive to copper (Buhl and Hamilton 1990).

Mercury, which is readily biomagnified in the foodweb, is also among the most toxic metals to fish. It occurs in some placer mining effluent at concentrations that could potentially result in a toxic hazard to young salmonids (Buhl and Hamilton 1991). At acute toxicity levels

(resulting in whole body residues of 5 to 7 mg/kg and liver residues of 26 to 68 mg/kg wet weight), gill flaring, increased frequency of respiratory movements, loss of equilibrium, and sluggishness are the first signs of mercury poisoning (Armstrong 1979 in Eisler 1987). At lower concentrations causing chronic toxicity, emaciation (from appetite loss), brain lesions, cataracts, inability to capture food or respond to light changes, and abnormal motor coordination are observed. More than 95% of the mercury concentrated in freshwater fish is toxic methylmercury, which is sequestered in muscle tissue for long-term storage, as well as in liver, kidney, and other organs (EPA 1980b; Eisler 1987).

### *Description of the Study Sites*

Figure 3 shows the sites of 1986 - 1988 studies. These sites are described as follows:

Site 1. Hogatza River immediately above its confluence with the Koyukuk River, at the northern boundary of Koyukuk Refuge (Latitude 66°00'00" N, Longitude 155°23'42" W; Township 7N, Range 16E, Section 24, NE 1/4, Kateel River Meridian). Samples were collected at the mouth of the Hogatza River from 1986 - 1988. The Hogatza River, 51 km (32 mi) west of Hughes, flows southwest for 192 km (120 mi), draining the watershed south of the continental divide, including the foothills of the Zane Hills. Tributaries to the Hogatza River include Caribou Creek (fed by Bear Creek and Dry Creek), Clear Creek (fed by Aloha Creek), and other streams. The Hogatza River is a meandering, typically clear-water river, subject to frequent high water events.

Site 2A. Koyukuk River at the northeastern boundary of the Koyukuk Refuge immediately west of Huggins Island, sampled in 1986 only (Latitude 65°53'19" N, Longitude 154°32'50" W; Township 5N, Range 20E, unnumbered section, Kateel R. Meridian). The meandering, low-gradient Koyukuk River heads at its Middle and North Forks, and flows southwest 680 km (424 mi) to the Yukon River. Approximately 480 km of the river flow through the refuge from its northeast to southwest corners. At Hughes, approximately 80 km (50 mi) to the southwest, the river is estimated to drain a watershed of approximately 48,433 km<sup>2</sup> (18,700 mi<sup>2</sup>). The Schwatka and Endicott mountains in the Brooks Range are a major source of runoff for the Koyukuk River. Flooding is common for the river, with high flows occurring after spring breakup in May and intermittently, depending on rainfall, through September.

Site 2B. Koyukuk River 8 km (5 mi) upstream from the Hogatza River at mouth of an unnamed slough, sampled in 1987 and 1988. This site is adjacent to a USFWS cabin (Latitude 65°56'21" N, Longitude 155°20'06" W; Township 6N, Range 17E, Section 8, SW 1/4, Kateel River Meridian) in the Koyukuk Refuge.

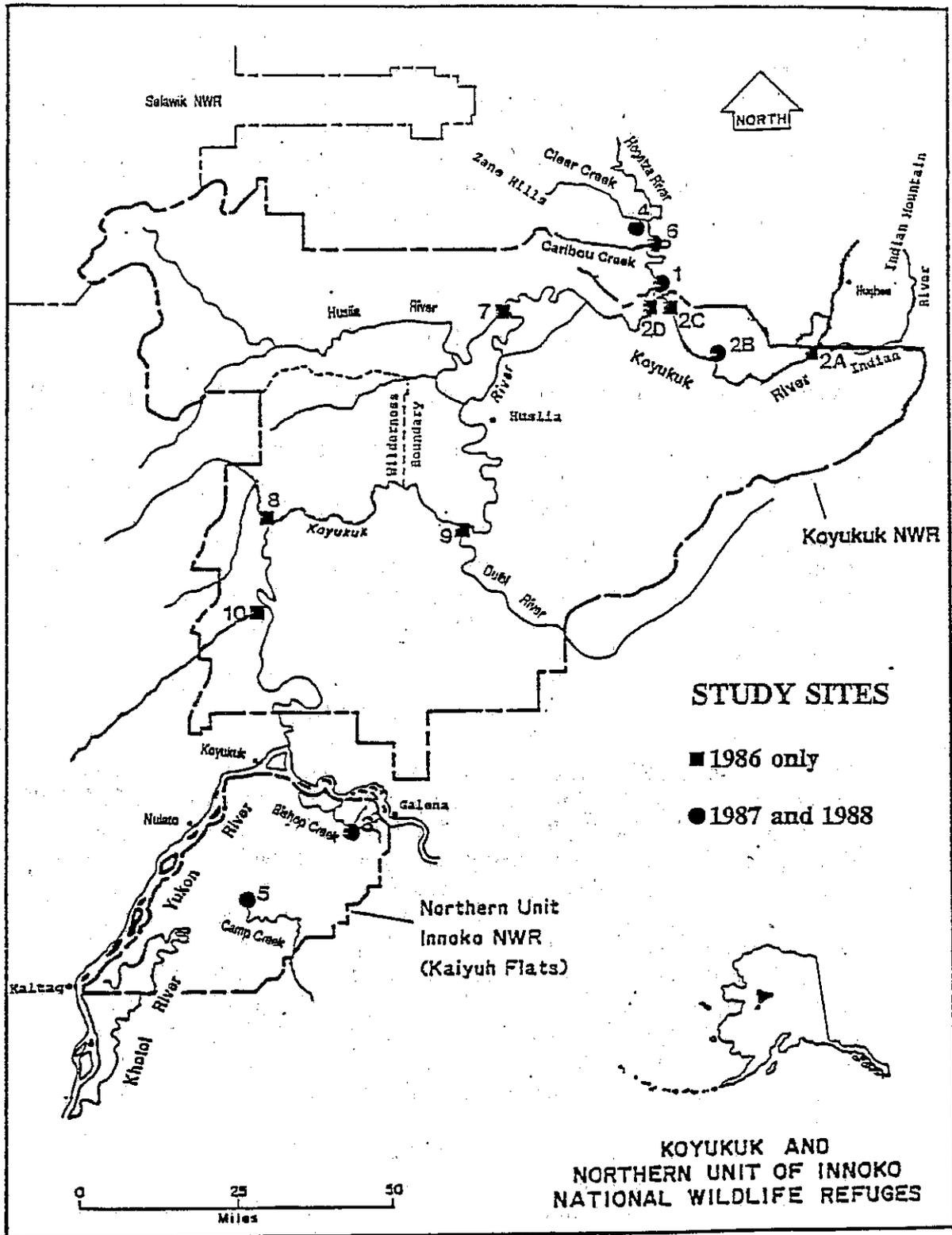


Figure 3. Study sites on Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge streams and rivers, 1986 - 1988.

Site 2C. Koyukuk River immediately upstream of confluence with the Hogatza River, sampled in 1986 (Latitude 65°59'59" N, Longitude 155°23'41" W; Township 7N, Range 16E, Section 24, SE 1/4, Kateel River Meridian) in the Koyukuk Refuge.

Site 2D. Koyukuk River immediately downstream of confluence with Hogatza River, sampled in 1986 (Latitude 65°59'59" N, Longitude 155°24'45" W; Township 7N, Range 16E, Section 24, NW 1/4, Kateel River Meridian) in the Koyukuk Refuge.

Site 3. Bishop Creek in the Northern Unit of the Innoko Refuge, approximately 16 km (10 mi) southwest of Galena, sampled in 1986, 1987, and 1988 (Latitude 64°40'00" N, Longitude 157°12'38" W; Township 9S, Range 8E, Section 35, NW 1/4, Kateel River Meridian). The sample site is on the south fork of Bishop Creek immediately before its confluence with the north fork of Bishop Creek, south of Pilot Mountain Slough, which connects Bishop Creek to the Yukon River. The site is approximately 25 km (16 mi) from the Galena Mine.

Site 4. Clear Creek near its the confluence with the Hogatza River (Latitude 66°13'06" N, Longitude 155°30'00" W; Township 10N, Range 16E, Section 32, SE 1/4, Kateel River Meridian), sampled in 1987 and 1988. This small creek meanders considerably from its headwaters at Caribou Mountain to the Hogatza River. Clear Creek appears to have been disrupted through past mining. Potential future mining on the creek, as well as on Aloha Creek, a tributary to Clear Creek, has been indicated.

Site 5. Bonanza Creek at the eastern entrance to Camp Lake (No. 105) in the southern portion of the Northern Unit of Innoko Refuge, sampled in 1986, 1987, and 1988 (Latitude 64°27'57"N, Longitude 157°43'18" W; Township 12S, Range 6E, Section 8, NW 1/4, Kateel River Meridian). Camp Creek, heading in the Kaiyuh Mountains to the east of the refuge, is a tributary to Bonanza Creek, which drains the Kaiyuh Flats, a wetlands complex, flowing through a series of lakes in the vicinity of the sample location, prior to draining into the Khotol River. The sample site is approximately 48 km (30 river miles) from the Camp Creek mine site just east of the refuge boundary.

Site 6. Caribou Creek near its confluence with the Hogatza River, sampled in 1987 and 1988 (Latitude 66°10'59" N, Longitude 155°26'59" W; Township 9S, Range 16E, Section 16, NE 1/4, Kateel River Meridian). Caribou Creek is a small creek originating in the Zane Hills and immediately northeast of the Koyukuk Refuge boundary. There is evidence of past mining along Caribou Creek, as well as current and past mining on two of its tributaries, Bear Creek and Dry Creek.

Site 7. Huslia River before its confluence with the Koyukuk River 21 km (13 mi) north of Roundabout Mountain in the Koyukuk River lowlands (Latitude

65°44'00" N, Longitude 156°33'27" W; Township 4N, Range 11E, Section 22, SW 1/4, Kateel River Meridian), sampled in 1986. The Huslia River is a small river formed by its north and south forks, flowing southeast for 88 km (55 mi) before joining the Koyukuk River.

Site 8. Kateel River before its confluence with the Koyukuk River 50 km (31 mi) southwest of Roundabout Mountain in the Koyukuk River lowlands (Latitude 65°27'24" N, Longitude 157°37'53" W; Township 1N, Range 6E, Section 28, SE 1/4, Kateel River Meridian), sampled in 1986. The Kateel River is a stream that flows northeast, then southeast for 184 km (115 mi) before joining the Koyukuk River. An Indian village or camp existed near this site in the mid-1800's.

Site 9. Dulbi River at its confluence with the Koyukuk River 10 km (6 mi) southeast of Roundabout Mountain in the Koyukuk River lowlands (Latitude 65°26'50" N, Longitude 156°31'27" W; Township 1N, Range 11E, Section 35, NW 1/4, Kateel River Meridian), sampled in 1986. The Dulbi River is a stream that flows northwest 194 km (121 mi) before joining the Koyukuk River.

Site 10. Gisasa River at its confluence with the Koyukuk River 61 km (38 mi) southwest of Roundabout Mountain in the Koyukuk River lowlands (Latitude 65°15'43" N, Longitude 157°40'56" W; Township 3S, Range 6E, Section 5, N 1/2, Kateel River Meridian), sampled in 1986. The Gisasa River is a stream that flows northeast 112 km (70 mi) to join the Koyukuk River.

The above sites include both mined and unmined drainages, but only mined drainages were studied in 1987 and 1988, when sampling of multiple environmental matrices occurred. Site 1, on the Hogatza River, receives placer mine effluent from Dry Creek and Bear Creek via Caribou Creek (Site 6), upstream of the Koyukuk Refuge. Further upstream, Clear Creek (Site 4), formerly mined, drains into the Hogatza River. Caribou Creek has been subject to extensive mining, some quite recent; however, Clear Creek showed few signs of recent mining during the study period. Site 3 (Bishop Creek) and Site 5 (Bonanza Creek), in the Northern Unit of the Innoko Refuge both receive drainage from mined sites east of the refuge.

Additional placer mining occurs on tributaries of the Koyukuk River upstream of the refuge. The heaviest concentration of mines is in the Wiseman area near the headwaters of the Koyukuk River. Sites 7, 8, 9, and 10 contain no known past history of mining. These sites were sampled only in 1986, when single grab samples of water for metal analysis were obtained.

## Materials and Methods

### *General*

Table 1 summarizes the types of samples collected at each sample site from 1986 through 1988.

Table 1. Samples collected from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge from 1986 - 1988. Numbers under each analysis category are site locations where collections were made.

Year	Water Quality	Dissolved Metals	Total Metals	Sediment Metals	Fish
1986	-	-	1-10	-	-
1987	1-6	1-6	1-6	1-6	1-6
1988	1-6	1-6	1-6	1-6	1-6

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

### *Collection Methods*

#### Water

Water quality samples were collected in 1987 and 1988. Samples for general water quality consisted of 500-ml or 1-L surface grab samples collected using polyethylene bottles that were triple-rinsed in the water to be sampled. Six different sites were sampled and river water was obtained at three different locations per site. Triplicate sampling was also performed using Nalgene® polyethylene bottles to obtain 1-L samples for total settleable solids and 500-ml samples for analysis of suspended solids. Grab samples were taken just below the surface, with each sample bottle extended into the current upstream of the collector to avoid contamination from resuspension of sediment or from the collector. Samples were either taken from alongshore or from near the shoreline from the float of a floatplane. Samples were filled to the top of the bottle to minimize gaseous exchange. Each sample was double-labelled and chilled in coolers following collection.

The pH of samples was measured within 12 hr of collection. Samples were analyzed within 24-hr for the following other water quality parameters: total alkalinity, total hardness, turbidity, conductivity, and settleable solids. Total hardness and alkalinity determinations were made using Hach hardness and alkalinity digital titration methods and color endpoints (Hach 1985). No phenolphthalein alkalinity was noted in any sample. Conductivity was measured with a Hach DREL/5<sup>®</sup> Conductivity Meter with automatic temperature compensation (conductivities adjusted to 25°C). Conductivity standards were used to check performance of this meter prior to each measurement series. The pH measurements were also made using a Hach<sup>®</sup> Digital pH Meter Model 19000 equipped with a combination electrode and automatic temperature compensation. Prior to each measurement series, two-buffer calibrations were performed using pH buffers accurate to  $\pm 0.01$  pH units which bracketed the pH of the samples.

Three different measures of solids in the water samples were also made during 1987 - 1988 studies concurrently with other water quality measurements. Turbidity was measured using a Hach<sup>®</sup> Portable Turbidity Meter Model 16800, calibrated with Hach Gelex<sup>®</sup> secondary standards for 1, 10, and 100 nephelometric turbidity units (NTU's). Total settleable solids were measured using the Imhoff Cone Method for 1-L samples (APHA et al. 1981). If settleable solids occurred, but did not exceed 0.1 ml/L, "trace" was recorded. Suspended solids (nonfilterable residue) were also measured on separate water samples submitted to Northern Testing Laboratories, Fairbanks, AK. EPA Method 160.2 (EPA 1983) was used for this determination.

During 1986 - 1988, water samples were also collected for the analysis of arsenic, mercury, and other trace elements. The 1986 and 1987 water samples consisted of grab samples collected in acid-rinsed 250-ml polyethylene bottles prepared by the collector. Only single grab samples were collected in 1986. In 1987 and 1988, three replicate samples were collected at each site. IChem<sup>®</sup> Series 200 high-density 250-ml or 500-ml polyethylene bottles with teflon lids precleaned for metals were used.

For 1987 and 1988, two types of water samples were collected in triplicate. Samples for analysis of total metals were collected in the same manner as the water quality samples. Samples for analysis of total dissolved metals samples were collected using a disposable 50-ml syringe to sample the river water directly. After each syringe was filled, two Nalgene<sup>®</sup> cellulose acetate LuerLock<sup>®</sup> filters, a 0.80  $\mu\text{m}$  prefilter and a 0.45  $\mu\text{m}$  filter, were piggybacked on the syringe tip and the sample was filtered directly into a 250- or 500-ml IChem<sup>®</sup> bottle. Approximately 120 ml were collected in this manner for each replicate sample.

## Sediments

Three sediment samples per site were obtained from each 1987 and 1988 study site where water samples were collected. Each sample was a composite grab sample from three adjacent

locations taken underwater, either from a shallow bank or from a floatplane or boat maneuvered close to shore. Sediments were collected in a 28-cm-wide stainless steel scoop (from accessible banks) or with a brass Ekman dredge (steep-banked sites), placed in a river-washed plastic container, homogenized with a clean glass or plastic rod, and transferred to a precleaned IChem<sup>®</sup> Series 200, 500- or 250-ml polyethylene bottle with a teflon lid using a stainless steel spoon. Surface samples (<10 cm deep) of silt, rather than sand or gravel, were selected to minimize bias in metal concentrations due to grain size. The sediment sampled was taken from a portion of the sample not in direct contact with the dredge or scoop.

## Fish

Fish were collected from refuge study sites in both 1987 and 1988 using experimental gill nets and spinning rods. Target fish species included adult Arctic grayling and northern pike. Other species were also obtained incidentally, including a broad whitefish, humpback whitefish, longnose sucker, and sheefish. Juvenile fish were also collected when insufficient adult fish were found. Fish were weighed with a Pesola<sup>®</sup> scale to the nearest gram, and total length and fork length were measured to the nearest millimeter.

### *Sample Handling and Labelling*

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

Field identifications, although unique for a given year, were not necessarily consistent with the study plans or between years. Prior to data interpretation, field identifications were therefore converted into a 10-digit identification number using designated alphanumeric fields, as described in Appendix B. This conversion was necessary to assure that samples collected from the same location were associated with a unique permanent sample location number, to identify samples taken in the same year, and to identify replicate samples at the same site within a given year. The sample identification also designates the type of sample: water, sediment, fish by species, and the type of water sample. The contaminants data for these samples were then entered into a contaminants data management system for northern and interior Alaskan samples, together with the 10-digit identification number using DBase IV<sup>®</sup> software.

All contaminants data entered into the data management system were proofed and corrected, if necessary, by comparing the original data sets with the hard-copy output. This proofing was performed by an independent party following initial data entry. In addition, the 1987 and 1988 data were screened for outliers by comparing replicate values for the same matrix and site. If two replicates were in close agreement, and the third replicate differed markedly and was in the zone of quantitative values, the third value was normally rejected unless duplicate analysis was used to confirm the value. For each year's data, mean values and standard deviations were computed for each analyte by matrix. Data for trace elements in water were also screened by comparing dissolved metal composition with total metal composition. Where dissolved metal composition equaled or exceeded total metal composition, contamination, either due to field or laboratory analytical procedures, is suspected and noted in the results section.

### *Laboratory Analyses*

Nitric acid-perchloric acid digestions were used on all matrices. Arsenic and antimony were analyzed by flameless atomic absorption spectrophotometry using hydride generation. Standard addition methods were employed for determining concentration. Mercury samples were digested with nitric acid using reflux condensers to prevent mercury loss, and were analyzed by cold vapor atomic absorption spectrophotometry. Other metals were analyzed with inductively coupled argon plasma spectroscopy (ICP) using preconcentration, with samples adjusted to pH 6.

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

A total metals analysis (strong digestion) was performed on both filtered and unfiltered water samples, as well as on tissue. However, only a weak digestion was performed on sediments to release metals that would potentially be available through biological processes. In some cases, very recoveries of sediment metals occurred. Only data with high recoveries ( $\geq 20\%$ ) met our quality assurance objectives, which included comparability with other published data on sediment metal concentrations (see *Quality Assurance/Quality Control* for information on the acceptability of each analyte by matrix).

### *Quality Assurance/Quality Control*

#### Field Collections

Prior to field sampling, refuge personnel involved in water quality and field contaminants sampling were trained by USFWS contaminant specialists in preparation for field studies.

A contaminants specialist accompanied refuge personnel during the 1987 sampling effort. Field collections were made using precleaned containers (IChem® Series 200) with protocols designated to reduce the potential of contaminating the samples. These included precautions to avoid direct contact between the sample container or sample and the collector or other sources of contamination (suspended sediment from the river bottom, airborne dust, metal such as aluminum boat or float plane surfaces, mosquito repellent, hand lotion, cigarette smoke, or airborne dust). Water quality sample containers were triple-rinsed in the river water prior to sampling.

During 1987 and 1988, three replicates of each sample type were collected at each site, with the exception of fish, where the target was five pike and five grayling. The latter goal was not met, especially in the case of grayling collections. However, the goal was usually met in the case of pike collections and multiyear sampling of fish has increased the confidence in the representativeness of the data presented for northern pike.

In other respects, field quality control procedures were followed. These included instrument calibrations or calibration checks prior to measurement of pH, conductivity, and turbidity; use of fresh reagents in titrations for hardness and alkalinity; and repeat analysis if a replicate sample deviated significantly from other measurements. Suspended solids measurements were also subject to performance checks using EPA check samples. The pH of samples was determined within 12 hr of sample collection; all other water quality analyses, except for total suspended solids, were performed within 24 hr of sample collection.

Sample preservation and handling was another area of emphasis in the sampling program. Sample locations and replicate numbers were preassigned for each drainage in the study plan. All samples were labelled both on the lids and on the bottles to reduce problems with label loss, illegibility, condensation-related ink smudges, and mixups once samples were opened by the laboratory. Water samples collected for trace element analysis were fixed with ultrapure nitric acid to a pH < 2 and kept refrigerated until submitted to the analytical laboratory. Water samples were packed in a separate cooler with ice packs for shipment to the laboratory by air courier.

Sediment sampling was performed using stainless steel, plastic and glass equipment. Samples were frozen following collection and shipped to the laboratory in coolers with dry ice by overnight air courier.

Following morphometric measurements, fish were rinsed with river water from the site of collection or distilled water to minimize external contamination. In 1987, large fish were wrapped in Saran Wrap®, followed by freezer wrap; small fish (usually < 300 gm) were placed in double Ziplock® bags. Fish were then frozen. The laboratory dissected the larger fish using carbon steel dissecting equipment and ultraclean conditions. Tissues collected from larger fish for analysis of trace elements included: dorsal muscle from the midsection (minus skin), whole liver, and whole kidney.

In 1988, dissection services were not offered by the laboratory, and were instead performed by the collector in the field. Dissections were performed with stainless steel and teflon dissection equipment on a clean surface, with new blades, rinsed in double-distilled water, used on each tissue sample. Tissues were immediately placed in precleaned IChem<sup>®</sup> Series 200 containers to reduce contamination and weighed in the tared container to reduce contaminant exposure. Samples were shipped to the laboratory in coolers with dry ice by overnight air courier and were frozen by the laboratory until analyses were performed.

## Laboratory Analysis

A full description of laboratory QA/QC procedures and screening criteria to accept or reject contaminants data is presented in Appendix C. Appendix D presents actual screening results for all analytes contained in the data sets, including results for analytes not accepted, method detection limits for rejected analytes, and the basis for rejection.

In summary, duplicate (split) samples, spiked samples, and standard reference materials (SRM's) were used to evaluate data quality. In 1987 and 1988, blank data were also provided by the laboratory, and criteria were applied to eliminate samples with significant contamination in the blanks. Tables 2 - 4 identify acceptable analytical data sets for water, sediments, and fish tissue analyses based on duplicate, spike, SRM, and blank criteria described in Appendix D, together with method detection limits for accepted analytes. The means by which contract laboratories defined method detection limits varied and should be considered approximate. The actual detection limit for each sample varied depending on sample weight, percent moisture, and chemical interferences present. Mercury analysis of water samples did not meet QC criteria, and also violated holding time requirements. APHA et al. (1989) stipulate analysis of water samples for mercury within 28 days of sample collection; none of the samples collected in this study were analyzed until at least 6 months following collection. Therefore, mercury data for water samples are not presented in the report.

Several assumptions were required when accepting or rejecting data. In 1988, no sediment spiked samples were analyzed by the laboratory. Therefore, the analytical performance on spikes from water and tissue spikes was used as a basis for screening laboratory spike recovery performance.

Values reported for an analyte that are less than twice the detection limit should be considered qualitative only. Values between 2 and 10 times the detection limit should be considered semi-quantitative (i.e., inherently prone to more variability than in the zone of quantitation, where measured values are greater than 10 times the detection limit).

Table 2. Acceptable data for metals analysis of water. Blank cells indicate unacceptable/missing data (poor spike or standard reference material recovery; poor precision within the zone of quantitation; and/or unacceptable levels of blank contamination). Shaded cells indicate duplicates had values less than twice the limit of detection (precision not estimated); otherwise, the data were acceptable.

WATER			Detection Limit (mg/L)		
Analyte	Method <sup>a</sup>	Matrix <sup>b</sup>	1986	1987	1988
Aluminum	ICPP	TM/DM			
Antimony	AA	TM/DM	0.0004		
Arsenic	AA	TM/DM	0.0005	0.001	0.003
Barium	ICPP	TM/DM		0.02	
Beryllium	ICPP	DM		0.002	
Cadmium	ICPP	TM/DM	0.0003	0.002	
Cobalt	ICPP	TM/DM		0.002	
Copper	ICPP	TM/DM	0.0008	0.007	
Iron	ICPP	TM/DM	0.239		
Lead	AA	TM/DM	0.007	0.025 <sup>d</sup>	
Magnesium	ICPP	TM/DM		0.25	
Manganese	ICPP	TM/DM		0.004	
Molybdenum	ICPP	TM	0.0006	0.02	
Nickel	ICPP	TM/DM	0.002	0.01	0.01
Selenium	ICPP/AA <sup>c</sup>	TM/DM	0.006		0.0025
Silver	ICPP	TM/DM		0.02	
Strontium	ICPP	TM/DM	0.003	0.003	
Thallium	ICPP/AA <sup>c</sup>	TM/DM	0.01	0.10	0.05
Tin	ICPP	DM		0.02	0.02
Vanadium	ICPP	TM/DM	0.0002	0.02	0.02
Zinc	AA/ICPP	TM/DM	0.001	0.005	0.005

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

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

<sup>c</sup> AA = 1987 and 1988

<sup>d</sup> Precision, measured by relative difference, was < 0.34, but > 0.17.

Table 3. Acceptable data for metals analysis of sediments. Blank cells indicate unacceptable/missing data (poor spike or standard reference material recovery; poor precision within the zone of quantitation; and/or unacceptable levels of blank contamination). Shaded cells indicate duplicates had values less than twice the limit of detection (precision not estimated); otherwise, the data were acceptable.

Analyte	SEDIMENT Method <sup>a</sup>	Detection Limit (mg/kg DW)	
		1987	1988 <sup>b</sup>
Ag	ICP	5.0	
As	AA	0.05 <sup>c</sup>	1.0
B	ICP	5.0	
Ba	ICP	5.0	0.5
Be	ICP	0.5	0.1
Cd	ICP	0.5	0.5
Cr	ICP	0.5	1.0
Cu	ICP	2.5	0.5
Mg	ICP	100	20
Mn	ICP	1.5	0.5
Mo	ICP	5.0	1.0
Ni	ICP	4.0	2.0
Pb	ICP	10.0	5.0
Sb	AA	0.025	
Sn	ICP	5.0	10
Sr	ICP	1.0	1.0
Tl	AA	0.2	
V	ICP	5.0	1.0
Zn	ICP	2.0	1.0

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

<sup>b</sup> Precision estimates based on water samples instead of sediment samples.

<sup>c</sup> Precision, measured by relative difference, was <0.34, but >0.17.

Table 4. Acceptable data for metals analysis of fish tissues. Blank cells indicate unacceptable/missing data (poor spike or standard reference material

Table 4. Acceptable data for metals analysis of fish tissues. Blank cells indicate unacceptable/missing data (poor spike or standard reference material recovery; poor precision within the zone of quantitation; and/or unacceptable levels of blank contamination). Shaded cells indicate duplicates had values less than twice the limit of detection (precision not estimated); otherwise, the data were acceptable.

FISH TISSUE		Detection Limit (mg/kg DW)	
Analyte	Method <sup>a</sup>	1987	1988 <sup>b</sup>
Ag	ICP	0.5	
Al	ICP		3.5
As	AA		0.5
B	ICP		2.0
Ba	ICP	0.5	0.5
Be	ICP	0.05	0.2
Cd	ICP	0.05	0.5
Cr	ICP	0.1	2.0
Cu	ICP		1.0
Fe	ICP		2.0
Mn	ICP	0.15 <sup>c</sup>	1.0
Mo	ICP		1.0
Ni	ICP	0.5	2.0
Pb	ICP	1.0	4.0
Sb	AA	0.025 <sup>c</sup>	5.0
Se	AA		1.0
Sn	ICP	0.50 <sup>c</sup>	5.0
Sr	ICP	0.1	2.0
Tl	AA	0.1	10.0
V	ICP	0.5	1.0

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

<sup>b</sup> Precision estimates based on water samples instead of tissue samples.

<sup>c</sup> Precision, measured by relative difference, was <0.34, but >0.17.

## Statistical Analysis

Data sets subjected to statistical analysis were transformed from the DBase IV® data management system to Lotus 3.1®, where files were reformatted, means and sample standard deviations computed, missing values replaced with -99, and values below the detection limit replaced by one-half the detection limit (as a more realistic approximation of the probable concentration). No mean was calculated if less than two thirds of the measured concentrations of a given analyte at a site were below the detection limit. The Lotus® compute function was used for computing pH logarithms and antilogs for statistical analysis of this parameter, for computing wet weight concentrations from dry weight concentrations of mercury in tissue samples, and for computations of fish condition index, using the formula:

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

where K is the condition factor (Ricker 1975).

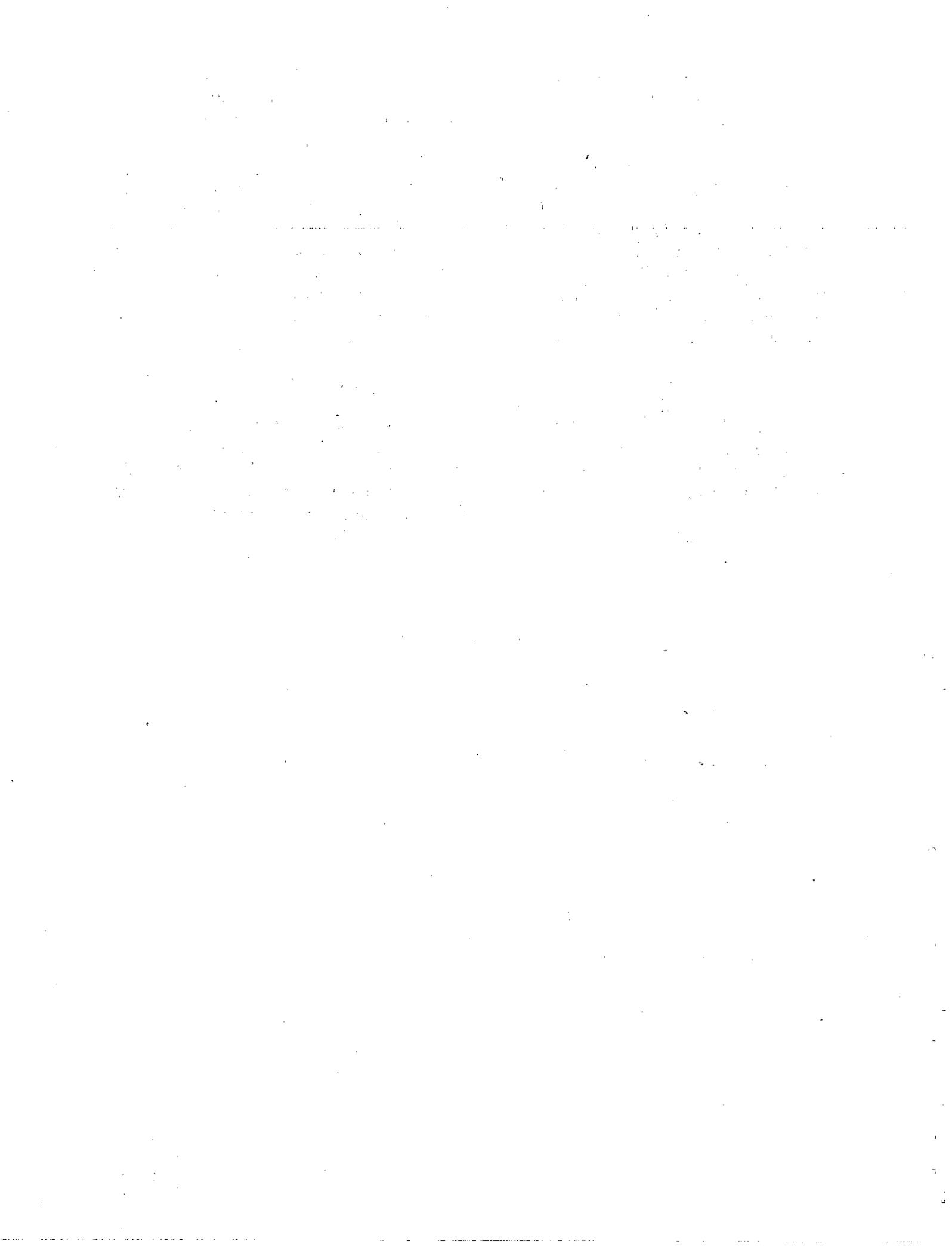
Scatterplots were also produced in Lotus to examine variable distributions, and associations among variables. Particular attention was devoted to inspection of the relationships between metal concentrations in fish tissue and fish length, weight, and condition index. Influences of metals on fish condition could be indicated by either linear or nonlinear decreases in condition with increasing metal concentration, or by bell-shaped distributions, depending on whether the metal is also a required trace element, with occurrence in limiting concentrations. Data for analytes with a majority of concentrations below the detection limit were eliminated from the data sets prior to statistical analysis. Remaining data were then imported into SPSS/PC+® statistical software for statistical analysis.

In most cases, samples sizes among groups were similar, based on the sample approach of collecting three replicate samples of water and sediment at each site and the target of five fish of the same species per site. (Only northern pike were collected in sufficient sample sizes to permit statistical comparisons; no statistical tests were performed on the nontarget species collected.) However, on occasion, examination of these data using Cochran's C test for homogeneity of variance (Dixon and Massey 1957) indicated that the variances were not homogeneous. Data sets also contained some variables which did not meet normality requirements for use of parametric statistics.

To assure that mean differences among sites, years, and matrices were not identified as significantly different as a result of artifacts relating to nonnormality, nonhomogeneity of variance, or the semi-quantitative nature of concentrations less than 10 times the detection limit, tests for differences among means were performed concurrently using parametric and nonparametric tests. One-way (single classification) analysis of variance for three or more samples with unequal sample sizes and unpaired or paired Student's t tests for two samples

were compared to analogous nonparametric tests, including the Kruskal-Wallis test for three or more samples and Mann-Whitney U tests for two-sample comparisons (Sokol and Rohlf 1981). For t-tests, a pooled variance estimate was used to calculate the t value when variances were not significantly different, and separate variance estimates were used when variances among groups differed significantly. Results of parametric and complementary nonparametric tests were then compared. Except when discussed, significant differences ( $P < .05$ ) or highly significant differences ( $P < .01$ ) were only reported when the results agreed. On some occasions, the probability level for the parametric test was just greater than 0.05, while the nonparametric test was just less than 0.05, or the converse was true. These results were reported and qualified. In almost every comparison, results from parametric and nonparametric comparisons yielded similar results. Therefore, a Scheffe multiple range test, a highly conservative parametric test for pairwise comparison of means (Sokol and Rohlf 1981), was then performed to identify differences among specific groups.

Correlations were examined using Pearson product-moment correlations for pairs of variables (Sokol and Rohlf 1981). The coefficient of determination,  $r^2$ , rather than the correlation coefficient,  $r$ , is presented in the text of this report, while  $r$  is presented in many of the tables. The former statistic is indicative of actual contribution to the variance, while the latter provides information on whether the relationship is positive or negative. To further examine the relationships of multiple variables correlated with a dependent variable, forward stepwise regressions (Sokol and Rohlf 1980) were employed using the named variables that were significantly correlated with the independent variable and SPSS/PC+<sup>®</sup> default criteria.



## Results

### Water

#### Water Quality

Table 5 presents water quality data for the 1987 - 1988 studies. The conductivity of the study sites, an indication of the total ions in the water, ranged widely, from 25 - 290  $\mu\text{S}/\text{cm}$ , depending on location and year. Significant differences among study sites were observed ( $F_{5,12} = 6889$ ,  $P \leq .01$ ), with conductivity being significantly higher in the Koyukuk River (Site 2) and in Bishop Creek (Site 3), than at Clear Creek (Site 4, 29 - 50  $\mu\text{S}/\text{cm}$ ) and Caribou Creek (Site 6, 25 - 41  $\mu\text{S}/\text{cm}$ ) ( $P \leq .05$ ) in 1987. The same pattern of differences in conductivity among sites was also observed in 1988. However, conductivity was significantly higher in 1988 than in 1987 (paired  $t = -3.27$ ,  $df = 5$ ,  $P \leq .05$ ). This is probably attributable to the lower water levels observed in 1988, in part due to lower discharge rates and evaporative losses associated with a later sampling date in five of six sites in 1988. As expected, conductivity was highly correlated ( $r^2 = .98$ ,  $df = 5$ ,  $P \leq .01$ ) with alkalinity, hardness, and pH in 1987 and with alkalinity and hardness ( $r^2 = .98$ ,  $df = 5$ ,  $P \leq .01$ ) in 1988.

The pH concentrations were near neutral, between 6.31 and 7.51 at all sites, with most sites being only slightly acidic in one or both years, indicating the absence of sulphide mineral concentrations near the surface or other disturbed areas. Differences in pH among sites were significant in both 1987 ( $F_{5,12} = 2616$ ,  $P \leq .01$ ) and 1988 ( $F_{5,12} = 289$ ,  $P \leq .01$ ). In 1987, the pH of Koyukuk River water was significantly higher than all other sites and the pH values of Sites 4 (Clear Creek) and 6 (Caribou Creek) were significantly lower than all other sites. In 1988, the pH of Site 3 (Bishop Creek) was higher than that of Site 2, and both these sites differed significantly from the remaining sites. Sites 4, 5 and 6 remained the sites lowest in pH, as would be expected of small streams draining spruce bog and other wetland areas. As expected, the pH measurements were highly correlated with alkalinity values in 1987 ( $r^2 = .96$ ,  $df = 5$ ,  $P \leq .01$ ), but not in 1988 ( $r^2 = .43$ ,  $df = 5$ ,  $P = .08$ ). Total alkalinity (the sum of carbonates, bicarbonates, and hydroxides) at the sites ranged from very low to moderate values. The Hogatza River (Site 1), Clear Creek (Site 4), Camp Creek (Site 5) and Caribou Creek (Site 6) were particularly low in alkalinity, both in comparison to Sites 2 and 3, and in actual alkalinity, indicating a poor buffering capacity and susceptibility to acidification events (e.g., snowmelt at breakup or acid rain) at these sites.

The total hardness, determined primarily by the concentration of calcium and magnesium ions, of the sites also differed significantly among sites. Sites 4 (Clear Creek) and 6 (Caribou Creek) were significantly lower in hardness than other sites in both 1987 and 1988. Total hardness values were highly correlated with total alkalinity in both years ( $r^2 = .99$ ,  $df = 5$ ,  $P \leq .01$ ), with the ratio of alkalinity to hardness ranging between 0.74 and 1.07 at each site. The data suggest that the sites are typical calcium/magnesium bicarbonate systems without substantial inputs of groundwater, organic matter from peat, or other sources of organic acids, sulfates, chlorides, or other ions.

Table 5. Water quality data for Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1987 - 1988. Each value is the mean for three replicate samples.

Site No.	Collection Date	Conductivity ( $\mu\text{S}/\text{cm}$ )	pH	Total Alkalinity (mg/L)	Total Hardness (mg/L)	Turbidity (NTU)	Settleable Solids (ml/L)	Suspended Solids (mg/L)
1	3 June 87	51	6.52	22.0	24.4	32.7	trace	28
2	3 June 87	150	7.51	56.6	76.6	63.7	1.7	107
3	4 June 87	146	7.41	64.7	77.1	6.0	trace	4.5
4	6 June 87	29	6.43	14.0	13.2	3.5	trace	12
5	5 June 87	95	6.96	39.3	49.6	5.3	trace	3.5
6	6 June 87	25	6.37	12.9	11.8	13.3	0.1	63
1	28 June 88 <sup>a</sup>	192	6.81	62.7	83.9	8.8	trace	16 <sup>b</sup>
2	28 June 88 <sup>a</sup>	290	6.94	105	141	9.3	trace	44 <sup>b</sup>
3	4 June 88 <sup>a</sup>	196	7.14	72.0	94.0	3.1	trace	14 <sup>b</sup>
4	30 June 88 <sup>a</sup>	50	6.31	21.0	21.0	1.3	ND <sup>c</sup>	34 <sup>b</sup>
5	2 July 88 <sup>a</sup>	175	6.75	62.1	77.6	3.8	trace	10 <sup>b</sup>
6	30 June 88 <sup>a</sup>	41	6.80	20.4	19.6	4.9	trace	13 <sup>b</sup>

<sup>a</sup> Analysis date presumed to be same as collection date, but date not recorded.

<sup>b</sup> Analyzed on 6/07/89

<sup>c</sup> ND = not detected

USGS data for the Koyukuk River at Hughes (upstream from Site 2) and at Bear Creek at the Hogatza River (actually Caribou Creek, Site 6) (USGS 1977) are in general agreement with these findings. However, USGS measured a higher bicarbonate alkalinity (45 mg/L) in August 1977 than we measured during our June sampling at the latter site. It is likely that this increase is the result of seasonal change.

Turbidity, a function of suspended clay, silt, organics, inorganics, and microorganisms in the water column, varied somewhat among sites and sample periods. However, turbidity was less than 7 NTU's at sites 3 - 5 in both years. Water samples from the Hogatza and Koyukuk rivers (Sites 1 and 2) were an order of magnitude more turbid (33 and 64 NTU's, respectively), significantly different ( $F_{5,12} = 153.99$ ,  $P < .01$ ) and higher (Scheffe test,  $P < .05$ ) than turbidity at the other sample sites in 1987. Site 2 also contained measurable settleable (1.7 ml/L) and high suspended solids (107 mg/L) in 1987. This amount of suspended solids is slightly higher than the amount reported as the maximum under normal Koyukuk River conditions (USFWS 1992), but the range of normal conditions within the Koyukuk Refuge has not yet been defined by an intensified sampling program. In 1988, the Hogatza and Koyukuk rivers experienced lower turbidities (8.8 and 9.3 NTU's, respectively), as well as lower suspended solids, but turbidities of these two sites were still significantly higher than the turbidity of Clear Creek (Site 4), which exhibited the lowest turbidity (Scheffe test,  $P < .05$ ). Both the Hogatza and Koyukuk rivers are subject to rapid changes in water levels and flooding. Elevated turbidities and suspended solids at these sites may be the result of differences in discharge rates and natural bank erosion among sites and within sites between years.

It is unclear to what extent the higher turbidities are related to accelerated erosion due to previous disturbance at mine sites, but mining influences, if present, appear small. Turbidities observed in the Hogatza River in 1984 (Deschermeier and Hawkinson 1985) were also low (5.7 - 6.2 NTU's), comparable to other study sites. Since Caribou Creek (Site 6) and Clear Creek (Site 4), previously mined tributaries to the Hogatza River, exhibited lower turbidities in both years than the Hogatza River, and since the Koyukuk River site was more than 100 km downstream from any mined tributaries, the turbidities observed at the sites appear unrelated to active mining. However, erosion from previous mine sites during prior rain events or breakup may have contributed to the solids burden at some of the sites.

#### Trace Elements

*Trace elements in 1986 study.* Quality assurance/quality control screening indicates that arsenic, copper, iron, nickel, lead, molybdenum, antimony, thallium, selenium, vanadium, and zinc data were acceptable for 1986 data sets. Table 6 shows results of trace element analysis for unfiltered water samples collected in September 1986 and analyzed for total metals.

Relatively high concentrations of iron occurred at most of the sites, a phenomenon observed in many other rivers in interior Alaska. Total iron in unfiltered water exceeded the EPA/State

drinking water criterion (0.3 mg/L) at 9 of 10 sites and the criterion for protection of freshwater life from chronic toxicity (1.00 mg/L) at all but three sites, assuming that this concentration occurs on four or more consecutive days per year. The highest concentration of iron (74.4 mg/L) was observed on the Koyukuk River at Site 2C, immediately upstream of the Hogatza River. This concentration was not observed in water samples from immediately upstream or downstream in the Koyukuk River, suggesting field contamination of this sample and/or laboratory error. Other metal concentrations, including arsenic, copper, nickel, antimony, vanadium, and zinc were also higher at Site 2C, sometimes by an order of magnitude, than samples both upstream and downstream from the site. Unfortunately, no replicate samples were collected during this year. Therefore, the source of the suspect values from Site 2C is unknown.

Table 6. Total metal concentrations in water from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1 September 1986. Concentrations are reported in mg/L.<sup>a</sup>

Site	As	Cu	Fe	Ni	Pb	Sb	V	Zn
1	0.0025	0.0058	7.29	0.008	<0.007	<0.0004	0.0120	0.0160
2A	0.0006	0.0020	0.55	0.003	0.007	<0.0004	0.0003	0.0063
2C	0.0210	0.0627	74.4	0.083	0.020	0.0009	0.0710	0.2230
2D	0.0020	0.0033	1.90	0.005	0.027	0.0004	0.0018	0.0077
3	<0.0005	0.0043	2.00	0.005	<0.007	<0.0004	0.0032	0.0091
5	<0.0005	0.0018	1.26	0.003	<0.007	<0.0004	0.0010	0.0030
7	<0.0005	0.0019	1.50	0.002	<0.007	<0.0004	0.0012	0.0031
8	0.0009	0.0026	0.52	<0.002	<0.007	0.0004	<0.0002	0.0014
9	<0.0070	0.0086	5.72	0.010	0.008	-	0.0061	0.0180
10	-	0.0088	0.24	<0.002	<0.007	-	<0.0002	0.0110

<sup>a</sup> Molybdenum, thallium and selenium were analyzed, but were not detected in any sample. Cadmium was detected in only one sample from Site 5 (Bonanza Creek) at 0.001 mg/L.

Arsenic and antimony were below detection levels or present at extremely low concentrations at all sites except 2C, as was nickel, antimony, vanadium, and zinc. Copper and zinc were

drinking water criterion (0.3 mg/L) at 9 of 10 sites and the criterion for protection of freshwater life from chronic toxicity (1.00 mg/L) at all but three sites, assuming that this concentration occurs on four or more consecutive days per year. The highest concentration of iron (74.4 mg/L) was observed on the Koyukuk River at Site 2C, immediately upstream of the Hogatza River. This concentration was not observed in water samples from immediately upstream or downstream in the Koyukuk River, suggesting field contamination of this sample and/or laboratory error. Other metal concentrations, including arsenic, copper, nickel, antimony, vanadium, and zinc were also higher at Site 2C, sometimes by an order of magnitude, than samples both upstream and downstream from the site. Unfortunately, no replicate samples were collected during this year. Therefore, the source of the suspect values from Site 2C is unknown.

Table 6. Total metal concentrations in water from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1 September 1986. Concentrations are reported in mg/L.<sup>a</sup> Shading indicates suspect data.

Site	As	Cu	Fe	Ni	Pb	Sb	V	Zn
1	0.0025	0.0058	7.29	0.008	<0.007	<0.0004	0.0120	0.0160
2A	0.0006	0.0020	0.55	0.003	0.007	<0.0004	0.0003	0.0063
2C	0.0210	0.0627	74.4	0.083	0.020	0.0009	0.0710	0.2230
2D	0.0020	0.0033	1.90	0.005	0.027	0.0004	0.0018	0.0077
3	<0.0005	0.0043	2.00	0.005	<0.007	<0.0004	0.0032	0.0091
5	<0.0005	0.0018	1.26	0.003	<0.007	<0.0004	0.0010	0.0030
7	<0.0005	0.0019	1.50	0.002	<0.007	<0.0004	0.0012	0.0031
8	0.0009	0.0026	0.52	<0.002	<0.007	0.0004	<0.0002	0.0014
9	<0.0070	0.0086	5.72	0.010	0.008	-	0.0061	0.0180
10	-	0.0088	0.24	<0.002	<0.007	-	<0.0002	0.0110

<sup>a</sup> Molybdenum, thallium and selenium were analyzed, but were not detected in any sample. Cadmium was detected in only one sample from Site 5 (Bonanza Creek) at 0.001 mg/L.

Arsenic and antimony were below detection levels or present at extremely low concentrations at all sites except 2C, as was nickel, antimony, vanadium, and zinc. Copper and zinc were present in all samples. Copper concentrations are typical of waters in urban areas, as well as mineralized waters, and below current EPA/State criteria for protection of aquatic life from chronic toxicity (0.012 mg/L for water at a total hardness of 100 mg/L as CaCO<sub>3</sub>). However, they are within published ranges for affecting sensitive species of algae, invertebrates, and fish (EPA 1980a; Buhl and Hamilton 1991, 1992). The only notable lead concentrations in the water samples were at Sites 2C (suspect) and 2D, on the Koyukuk River upstream and downstream of the mouth of the Hogatza River.

Vanadium was present at 8 of 10 sample sites. No literature is available on typical vanadium concentrations in unfiltered Alaskan waters and few data are available on total vanadium in rivers elsewhere. Concentrations at most sites resemble those in average river water (0.0009 mg/L) (Skinner and Turekian 1973 in Waldichuk 1974), freshwaters generally (0.001 mg/L) (Jenkins 1981), and tap water samples nationwide (.0043 mg/L) (Lagerkvist et al. 1986). However, concentrations at Sites 1, 2C (a suspect sample), 3, and 9 are higher. The Site 1 concentration of 0.012 mg/L is in the range of an unpublished EPA advisory value for protection of aquatic life (USFWS 1988).

*Trace elements in 1987 study.* In 1987, replicate sampling for total metals and dissolved metals was conducted at six sites on Koyukuk Refuge and the Northern Unit of Innoko Refuge. Sampling focused on sites with potential or existing mine sites. Results for these analyses are presented in Tables 7 and 8.

Quality assurance/quality control screening of water samples indicated that arsenic, beryllium, cadmium, chromium, copper, lead, magnesium, manganese, molybdenum, nickel, silver, strontium, thallium, tin, vanadium, and zinc data sets met screening criteria. However, many of these metals, including cadmium and chromium were found in concentrations near the detection limit, where precision and accuracy are expected to be low. Results of paired t-tests and Mann-Whitney U tests comparing total metals and dissolved metals generally paralleled one another and disclosed no significant differences in concentrations of total versus dissolved barium, magnesium, manganese, and zinc, as would be expected in waters of relatively low suspended solids content. The equivalency of these results suggests that these trace elements are present mostly in the dissolved form.

Dissolved cadmium and lead were significantly higher ( $P \leq .05$ ) than total cadmium and lead. Dissolved chromium was also higher than total chromium, a difference that was significant in the Mann-Whitney U test ( $Z = -2.88$ ,  $df = 5$ ,  $P \leq .01$ ), but not quite significant in the paired t-test ( $t = 2.27$ ,  $df = 5$ ,  $P = .07$ ). Significant positive linear correlations were also noted between the dissolved and total concentrations of lead and cadmium, respectively, but not between dissolved and total chromium. These results, taken together, suggest filter contamination. Filter contamination by cadmium or a systematic laboratory error in the analysis of dissolved or total cadmium and lead. (There is also possible evidence of some

Table 7. Total metal concentrations in water from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1987. Concentrations are reported in mg/L.<sup>a</sup>

Site	Date	Ba	Cd	Cr	Pb	Mg	Mn	Sr	Zn
1	3 June	0.030	0.006	0.006	0.150	1.72	0.040	0.030	0.010
		<0.020	0.006	0.006	0.192	1.62	0.038	0.028	0.008
		0.020	0.006	0.005	0.177	1.48	0.036	0.025	0.112
$\bar{x}$	0.020	0.006	0.006	0.173	1.61	0.038	0.028	0.043	
2B	3 June	0.030	0.006	0.007	0.139	5.05	0.103	0.067	0.022
		<0.020	0.003	0.003	0.072	2.45	0.037	0.036	0.008
		0.020	0.006	0.006	0.107	5.05	0.090	0.068	0.030
$\bar{x}$	0.020	0.005	0.005	0.106	4.18	0.077	0.057	0.020	
3	4 June	0.040	0.004	0.004	0.154	4.02	0.024	0.068	0.017
		0.030	0.003	<0.002	0.086	2.40	0.014	0.041	0.020
		0.020	0.002	0.002	0.092	1.85	0.011	0.031	0.020
$\bar{x}$	0.030	0.003	0.003	0.111	2.76	0.016	0.047	0.019	
4	6 June	0.020	0.002	0.005	0.061	0.75	0.036	0.013	0.031
		<0.020	0.002	<0.004	0.058	0.30	0.005	0.008	<0.005
		<0.020	0.002	0.004	0.069	0.28	0.004	0.007	0.010
$\bar{x}$		0.002	0.004	0.063	0.44	0.015	0.009	0.014	
5	5 June	<0.020	0.002	0.002	0.094	1.50	0.015	0.018	0.010
		<0.020	0.002	0.004	0.068	1.18	0.012	0.014	0.038
			0.002	0.003	0.081	1.34	0.014	0.016	0.024
$\bar{x}$		0.003	0.004	0.091	0.50	0.017	0.008	0.014	
6	6 June	<0.020	0.003	<0.002	0.084	0.52	0.020	0.010	0.013
		<0.020	0.003	0.005	0.086	0.42	0.016	0.009	0.006
			0.003	0.003	0.087	0.48	0.018	0.009	0.011
$\bar{x}$		0.003	0.003	0.087	0.48	0.018	0.009	0.011	

<sup>a</sup> Ag, As, Be, Cu, Mo, Sn, and Tl were not detected in any sample. Ni and V were detected in only one sample (see text).

<sup>b</sup> Means were computed using 1/2 the detection limit for a nondetect if remaining replicate concentrations of an analyte were positive.

Table 8. Dissolved metal concentrations in water from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1987. Concentrations are reported in mg/L.<sup>a</sup> Shading indicates suspect data.

Site	Date	Ba	Cd	Cr	Pb	Mg	Mn	Sr	Zn
1	6/03/87	<0.02	0.012	<0.002	0.386	1.52	0.014	0.029	0.008
		<0.02	0.008	0.013	0.307	1.48	0.014	0.028	0.020
		<0.02	0.014	0.016	0.415	1.45	0.014	0.028	0.015
2B	6/03/87	-	0.011	0.010	0.369	1.48	0.014	0.028	0.014
		<0.02	0.012	<0.002	0.258	4.90	0.012	0.075	0.057
		<0.02	0.010	0.010	0.306	4.92	0.009	0.077	0.018
3	6/04/87	<0.02	0.012	0.016	0.409	4.58	0.022	0.072	0.016
		-	0.011	0.009	0.324	4.80	0.014	0.075	0.030
		0.05	0.008	<0.010	0.247	4.72	<0.004	0.079	0.134
4	6/06/87	0.05	0.007	0.008	0.236	4.88	<0.004	0.084	0.012
		0.05	0.010	0.011	0.332	4.50	<0.004	0.078	0.018
		0.05	0.008	0.010	0.272	4.70	-	0.080	0.055
5	6/05/87	<0.02	0.007	0.010	0.250	0.72	0.012	0.020	0.009
		<0.02	0.009	0.012	0.341	0.72	0.006	0.020	0.014
		-	0.009	0.009	0.316	0.70	0.005	0.020	0.041
6	6/06/87	<0.02	0.008	0.010	0.296	0.71	0.008	0.020	0.021
		<0.02	0.007	0.100	0.300	3.32	0.023	0.040	0.022
		<0.02	0.008	0.008	0.289	3.30	0.024	0.039	0.020
6	6/06/87	<0.02	0.008	0.010	0.268	3.23	0.022	0.040	0.012
		-	0.008	0.009	0.286	3.30	0.023	0.040	0.018
		<0.02	0.008	0.010	0.143	0.60	0.016	0.017	0.006
6	6/06/87	0.02	0.009	0.115	0.340	0.62	0.020	0.018	0.053
		<0.02	0.010	0.012	0.340	0.62	0.016	0.018	0.012
		-	0.009	0.046	0.274	0.61	0.017	0.018	0.024

<sup>a</sup> Ag, As, Be, Ni, Sn and Tl were not detected in any sample. V was detected in only one sample (see text).

<sup>b</sup> Means were computed using 1/2 the detection limit for a nondetect if remaining replicate concentrations of an analyte were positive.

magnesium contamination or systematic error at Site 5, since dissolved magnesium concentrations were three times higher than total magnesium concentrations.) Alternatively, the dissolved samples may have been subjected to a more rigorous digestion due to addition of more acid to these samples during field preservation. A volume of 0.75 mL Ultrix<sup>®</sup> nitric acid was added to each 250-ml total metals sample and to each 120- to 150-ml dissolved metals sample. Thus, dissolved metal samples received up to twice as much acid. The ratio of dissolved metal to total metal concentration averaged 2.7 for cadmium and 3.2 for lead. These ratios are higher than would be expected if direct contamination by the acid had occurred. However, as a result of questions concerning the validity of analyses for cadmium, lead, and chromium in the 1987 samples, data for these metals are not interpreted further.

One-way analysis of variance tests, together with the Scheffe procedure, showed significant among-site differences in total magnesium, manganese, and strontium. Site 2 (Koyukuk River) water samples contained significantly more magnesium ( $\bar{x} = 4.18$  mg/L) than Sites 4 (Clear Creek) and 6 (Caribou Creek) ( $\bar{x} = 0.44$  and  $0.48$  mg/L, respectively). Similarly, Site 2 water samples contained significantly more manganese ( $\bar{x} = 0.08$  mg/L) than Sites 3, 4, 5, and 6 (range of  $\bar{x} = 0.01 - 0.02$  mg/L), and significantly more strontium ( $\bar{x} = 0.057$  mg/L) than Sites 4 and 6 ( $\bar{x} = 0.009$  mg/L at both sites). The mean concentration of total magnesium was highly correlated with conductivity ( $r^2 = .82$ ,  $df = 5$ ,  $P \leq .01$ ); pH ( $r^2 = .82$ ,  $df = 5$ ,  $P \leq .01$ ); alkalinity ( $r^2 = .74$ ,  $df = 5$ ,  $P \leq .05$ ); hardness ( $r^2 = .80$ ,  $df = 5$ ,  $P \leq .01$ ), and turbidity ( $r^2 = .55$ ,  $df = 5$ ,  $P \leq .05$ ). Strontium showed a similar pattern of positive correlation with conductivity ( $r^2 = .80$ ,  $df = 5$ ,  $P \leq .01$ ); pH ( $r^2 = .78$ ,  $df = 5$ ,  $P = .01$ ); alkalinity ( $r^2 = .75$ ,  $df = 5$ ,  $P \leq .05$ ); and hardness ( $r^2 = .78$ ,  $df = 5$ ,  $P \leq .01$ ), while manganese concentrations were not significantly correlated with any water quality variable. Since magnesium and strontium were strongly correlated ( $r^2 = .96$ ,  $df = 5$ ,  $P = .01$ ), and since both divalent ions contribute to hardness, these relationships are expected.

Significant differences in dissolved metals were also observed among sites that paralleled the results for total metals. Magnesium and strontium concentrations were significantly lower at Site 4 (Clear Creek) and at Site 6 (Caribou Creek), which formed a homogeneous subset, than at the other sites. Strontium concentrations were significantly higher at Sites 2 (the Hogatza River) and magnesium and strontium were significantly higher at Site 3 (Bishop Creek) than at other sites. However, Site 3 was significantly lower in manganese than all sites except Site 4. No significant differences occurred in zinc concentrations among sites. Barium concentrations were not statistically compared due to the preponderance of concentrations below the detection limit.

*Trace elements in 1988 study.* Quality assurance screening indicated that aluminum, arsenic, cadmium, chromium, copper, iron, lead, nickel, selenium and thallium data are acceptable for the total metals analysis in the 1988 data set. Similarly, dissolved aluminum, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, thallium and tin data are also acceptable in the 1988 data set. Contrary to our instructions to the laboratory, no mercury analysis was conducted on total metals samples. However, the mercury analysis for

dissolved metals violated prescribed holding times and is therefore rejected on this basis in any case.

Tables 9 and 10 show results of total and dissolved metals analysis of water, respectively, for samples collected in late June and early July 1988. No selenium or thallium was detected in any total metals sample, and arsenic was detected in only one of three replicates at Site 3 at a trace concentration of 0.0065 mg/L. Thallium was detected in two dissolved metal samples, in one of three replicates each from Sites 1 and 4, at 0.022 and 0.028 mg/L, respectively. These positives for thallium are questionable, since they were not confirmed in replicates, and since there is no indication of thallium in any total metals sample. Tin was also detected in two dissolved metal samples, at 0.006 mg/L in one replicate from Site 3 and at 0.0061 mg/L in one replicate from Site 1. These concentrations are close to the detection limit for tin, and probably indicate the presence of tin, based on tin occurrence in most total metal samples in concentrations of the same order of magnitude. The latter results did not, however, pass quality control screening.

Aluminum was present in all water samples, both in the total and dissolved form. Mean total aluminum tended to be higher than mean dissolved aluminum concentrations at the six sites, but not significantly so (paired  $t = -1.23$ ,  $df = 5$ ,  $P \leq .27$ ). Total and dissolved concentrations of other metals also did not differ significantly; however, total copper was usually higher than dissolved copper, while chromium, iron, and nickel concentrations were almost identical, suggesting that most of these metals were present primarily in the dissolved form.

Small, but significant differences were found among sites in total aluminum ( $F_{5,12} = 27.2807$ ,  $P \leq .01$ ) and dissolved aluminum ( $F_{5,11} = 3.1248$ ,  $P \leq .05$ ), using one-way analysis of variance, but differences were not significant when Kruskal-Wallis one-way analysis of variance was used ( $\chi^2 = 7.55$ ,  $P = .18$  for total aluminum;  $\chi^2 = 9.6013$ ,  $P = .09$  for dissolved aluminum). Total aluminum was higher at Site 1 (the Hogatza River) than at all other sampled sites. Mined tributaries to the Hogatza River had significantly lower concentrations than the Hogatza River, but were higher in aluminum concentration than remaining sites.

Significant differences among sites were also observed in total iron ( $F_{5,12} = 22.7341$ ,  $P \leq .01$ ) and dissolved iron ( $F_{5,12} = 138.1177$ ,  $P \leq .01$ ), and these differences were confirmed in Kruskal-Wallis tests. Site 1 (the Hogatza River) contained significantly more total iron ( $\bar{x} = 1.25$  mg/L) than the remaining sites, and Site 5 (Bonanza Creek) was also significantly higher in total iron than the site with the lowest concentration, Site 4, Clear Creek. Sites 1 and 5 were also significantly higher in dissolved iron than the remaining sites. Total nickel also differed significantly among sites ( $F_{5,12} = 3.4329$ ,  $P \leq .05$ ), but no two sites were distinguished using the Scheffe procedure.

*Comparison of trace element concentrations among years.* Total zinc concentrations at the sample sites in 1986 and 1987 were compared using a paired t-test. No significant differences in the concentration of zinc at the sites was observed between years.

Table 9. Total metal concentrations in water from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1988. Concentrations are reported in mg/L.<sup>a,b</sup>

Site	Date	Al	Cd	Cr	Cu	Fe	Ni	Pb
1	28 June	0.369	<0.0002	0.004	0.0043	1.070	0.0026	0.0035
		0.335	<0.0002	0.005	0.0070	1.110	0.0042	<0.0023
		0.388	0.0005	0.004	0.8040	1.570	0.0039	0.0039
	$\bar{x}$	0.364	-	0.004	0.2720	1.250	0.0036	0.0029
2B	28 June	0.070	0.0007	0.004	0.0077	0.375	0.0027	0.0061
		0.120	0.0003	0.003	0.0059	0.428	0.0041	0.0038
		0.018	<0.0002	0.004	0.0050	0.232	<0.0018	0.0077
	$\bar{x}$	0.069	0.0004	0.004	0.0060	0.345	0.0026	0.0060
3	4 June	0.067	0.0003	0.003	0.0056	0.207	0.0023	0.0029
		0.078	0.0004	0.003	0.0044	0.286	0.0027	<0.0023
		0.085	<0.0002	0.003	0.0056	0.323	0.0034	0.0023
	$\bar{x}$	0.077	0.0003	0.003	0.0050	0.272	0.0028	0.0021
4	30 June	0.075	0.0003	0.004	0.0056	0.144	0.0023	0.0064
		0.109	<0.0002	0.003	0.0012	0.158	<0.0018	0.0144
		0.046	<0.0002	0.003	0.0059	0.093	<0.0018	<0.0023
	$\bar{x}$	0.077	-	0.003	0.0040	0.132	-	0.0073
5	2 July	0.072	<0.0002	0.003	0.0054	0.673	0.0040	<0.0023
		0.108	0.0018	0.006	0.0077	0.867	0.0052	0.0050
		0.020	0.0007	0.004	0.0056	0.506	0.0038	0.0028
	$\bar{x}$	0.067	0.0009	0.004	0.0060	0.682	0.0043	0.0030
6	30 June	0.071	0.0003	0.002	0.0020	0.223	<0.0018	<0.0023
		0.070	0.0002	0.003	0.0044	0.204	<0.0018	<0.0023
		0.161	<0.0002	0.003	0.0043	0.395	0.0032	<0.0023
	$\bar{x}$	0.101	0.0002	0.003	0.0040	0.274	-	-

<sup>a</sup> Se and Tl were not detected in any sample; As was detected in one sample.

<sup>b</sup> Means were computed using ½ the detection limit for a nondetect if remaining replicate concentrations of an analyte were positive.

Table 10. Dissolved metal concentrations in water from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1988. Concentrations are reported in mg/L.<sup>a</sup>

Site	Date	Al	Cd	Cr	Cu	Fe	Ni	Pb
1	28 June	0.168	<0.0002	0.006	0.007	0.916	0.004	0.006
		0.081	<0.0002	0.007	0.011	0.763	0.003	0.003
		0.139	<0.0002	0.008	0.006	0.840	0.009	0.003
	$\bar{x}$	0.129	-	0.007	0.008	0.840	0.005	0.004
2B	28 June	0.015	0.0004	0.004	0.022	0.085	0.001	<0.002
		0.048	0.0002	0.003	0.007	0.143	0.003	<0.002
		0.095	0.0006	0.003	0.006	0.115	0.003	<0.002
	$\bar{x}$	0.052	0.0004	0.003	0.012	0.114	0.002	-
3	4 June	0.029	<0.0002	0.001	0.006	0.234	0.003	<0.002
		0.065	0.0006	0.005	0.011	0.248	0.004	<0.002
		$\bar{x}$	0.047	-	0.003	0.008	0.241	0.003
4	30 June	0.076	<0.0002	0.002	0.006	0.147	0.001	<0.002
		0.087	<0.0002	0.002	0.005	0.145	0.002	<0.002
		0.129	<0.0002	0.003	0.006	0.114	0.001	<0.002
	$\bar{x}$	0.108	-	0.003	0.005	0.130	0.002	-
5	2 July	0.061	<0.0002	0.002	0.006	0.815	0.004	<0.002
		0.048	<0.0002	0.003	0.007	0.938	0.003	0.010
		0.048	<0.0002	0.002	0.005	0.792	0.004	<0.002
	$\bar{x}$	0.052	-	0.003	0.006	0.865	0.004	-
6	30 June	0.124	<0.0002	0.003	0.005	0.287	0.003	<0.002
		0.089	0.0004	0.005	0.011	0.309	0.004	<0.002
		0.069	0.0150	0.003	0.006	0.267	0.001	0.232
	$\bar{x}$	0.079	0.0052	0.004	0.009	0.288	0.002	-

<sup>a</sup> Se was not detected in any sample; Sn and Tl were detected in two samples, but thallium concentrations were suspect (see text).

<sup>b</sup> Means were computed using 1/2 the detection limit for a nondetect if remaining replicate concentrations of an analyte were positive.

Similarly, total copper, iron and nickel concentrations at the sample sites in 1986 and 1988 were compared, and no significant differences between years were observed at the sites. Statistical comparisons of other metals were not made, since these were frequently present below the detection limit, or considered valid in only one of the three years sampled.

### *Sediments*

#### Trace Elements in 1987 Study

Metals identified as acceptable from quality control screening of 1987 sediment analyses included antimony, beryllium, boron, copper, lead, molybdenum, nickel, silver, strontium, tin, and arsenic (Table 11). Silver and tin were not detected in any sample. Molybdenum was detected in only two samples, in one replicate from Site 3 at 3.6 mg/kg, and in one replicate at Site 6 at 8.8 mg/kg. Similarly, boron was detected in one or two replicates at Sites 2 - 5, but not at Sites 1 or 6. Lead was also sporadically detected in sediment samples at concentrations from 18 to 24 mg/kg. These concentrations are not particularly high for sediment metal concentrations analyzed as total metals (Moore and Ramamoorthy 1984). However, the incomplete digestions employed by the analytical laboratories may slightly underestimate total lead. The above metals generally occurred in the qualitative range of measurement (less than twice the detection limit), and high variability in this range is expected.

Antimony, copper, nickel, strontium, and arsenic occurred in all sediment samples. Mean metal concentrations at the sites in mg/kg dry weight were antimony, 0.278- 0.447; copper, 16.0 - 32.5; nickel, 15.2 - 33.5; strontium, 13.7 - 40.2; and arsenic 5.47 - 12.97. No significant differences were observed in antimony concentrations among sites using one-way analysis of variance. Significant differences were found in the concentrations of copper, nickel, strontium, and arsenic concentrations among sites using a one-way analysis of variance. For copper, differences among sites were highly significant ( $F_{5,12} = 6.6905$ ,  $P \leq .01$ ). Copper concentrations were highest ( $\bar{x} = 32.5$  mg/kg) at Site 5, Bonanza Creek, and significantly lower at Site 4, Clear Creek ( $\bar{x} = 16.0$  mg/kg) and Site 6, Caribou Creek ( $\bar{x} = 19.8$  mg/kg). For nickel, differences among sites were also highly significant ( $F_{5,12} = 6.0065$ ,  $P \leq .01$ ), with nickel at Site 5 ( $\bar{x} = 33.5$  mg/kg) significantly higher than nickel concentrations at Site 4 ( $\bar{x} = 15.2$  mg/kg), with the lowest concentration. Other sites did not differ significantly from these sites.

Among-site differences in strontium were also significant ( $F_{5,12} = 14.5905$ ,  $P \leq .01$ ), with strontium significantly higher at Site 2 ( $\bar{x} = 40.2$  mg/kg), the Koyukuk River, than at Sites 1, 4, 5, and 6 ( $\bar{x} = 13.7 - 24.9$  mg/kg). Site 3 ( $\bar{x} = 29.6$  mg/kg), Bishop Creek, was also significantly elevated in sediment strontium in comparison to Site 1.

Table 11. Metal concentrations in sediment from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1987. Concentrations are reported in mg/kg dry weight.<sup>a</sup>

Site	Date	As	Be	B	Cu	Pb	Mo	Ni	Sb	Sr
1	3 June	6.94	<0.9	<8.7	26.7	18.8	<8.7	28.0	0.273	18.8
		7.23	<1.0	<9.5	17.8	<19.0	<9.5	13.8	0.312	10.0
		6.71	<1.0	<9.4	16.0	<19.0	<9.4	17.5	0.304	12.3
	$\bar{x}$	6.96	-	-	20.2	-	-	19.8	0.296	13.7
2B	3 June	11.30	<0.9	<9.2	28.2	<18.3	<9.2	28.0	0.352	41.4
		13.70	<1.0	15.0	28.9	<19.0	<9.5	30.4	0.390	40.9
		12.00	<0.9	<9.0	21.1	<17.9	<9.0	24.2	0.412	38.2
	$\bar{x}$	12.33	-	-	26.1	-	-	27.5	0.385	40.2
3	9 July	5.81	<0.8	<7.8	18.9	<15.5	3.6	18.4	0.285	22.2
	19 July	5.23	<1.0	15.0	28.9	<19.0	<9.5	30.4	0.300	40.9
	19 July	5.38	<0.8	13.4	19.4	<15.9	<8.0	18.8	0.250	25.6
	$\bar{x}$	5.47	-	10.8	22.4	-	-	22.5	0.278	29.6
4	6 June	8.31	0.9	10.8	18.2	18.0	<9.0	18.0	0.317	17.4
		6.90	<1.1	<10.3	14.9	22.7	<10.3	14.7	0.661	15.3
		7.81	<1.0	16.1	14.9	<20.7	<10.3	13.0	0.364	15.3
	$\bar{x}$	7.67	-	10.7	16.0	17.0	-	15.2	0.447	16.0
5	18 July	12.40	<1.1	<10.8	32.0	<21.6	<10.8	33.0	0.374	24.0
		13.40	<1.1	<10.7	33.0	<21.3	<10.7	31.5	0.362	24.7
		13.10	1.0	30.0	32.5	24.0	<9.9	36.1	0.333	26.0
	$\bar{x}$	12.97	-	-	32.5	-	-	33.5	0.356	24.9
6	6 June	8.06	<0.8	<8.0	18.0	<16.7	<8.0	20.7	0.287	15.4
		8.67	<0.9	<8.8	21.2	19.4	8.8	21.7	0.317	17.9
		8.62	<0.8	<7.9	20.3	<15.8	<7.9	21.5	0.291	16.8
	$\bar{x}$	8.45	-	-	19.8	-	-	21.3	0.298	16.7

<sup>a</sup> Ag and Sn were not detected in any sample.

<sup>b</sup> Mean concentrations were computed using  $\frac{1}{2}$  the detection limit for a nondetect if remaining replicate concentrations of an analyte were positive.

Arsenic differences among sites were also pronounced ( $F_{5,12} = 63.7174$ ,  $P \leq .01$ ), with the highest concentrations at Sites 2 and 5 ( $\bar{x} = 12.3$  and  $13.0$  mg/kg, respectively) and significantly lower concentrations at the remaining sites ( $\bar{x} = 5.5 - 8.4$  mg/kg).

Table 12 shows correlations among sediment metals consistently present in the 1987 data set. No significant correlation was observed between antimony and any other metal, but positive, significant relationships among the other metals are present. The most notable strong relationship is that between copper and nickel ( $r^2 = .93$ ,  $df = 17$ ,  $P \leq .01$ ).

Table 12. Correlation matrix for 1987 sediment metals from six refuge river sites, with three replicates per site. Significant correlation coefficients ( $r$ ) are presented for one-tailed tests.

Element	Sb	Cu	Ni	Sr
Sb				
Cu	-.1124			
Ni	-.1079	.9681**		
Sr	.0411	.6060**	.6340**	
As	.2202	.6611**	.6637**	.4311

\* 0.01 probability level

\*\* 0.001 probability level

Correlations were also examined between mean site concentrations of antimony, copper, nickel, strontium, and arsenic and mean water quality values at the sites using Pearson-Moment linear correlation. Strontium concentrations in sediments were significantly correlated with conductivity ( $r^2 = .84$ ,  $df = 5$ ,  $P \leq .01$ ), pH ( $r^2 = .89$ ,  $df = 5$ ,  $P \leq .05$ ), total alkalinity ( $r^2 = .76$ ,  $df = 5$ ,  $P \leq .05$ ), and total hardness ( $r^2 = .83$ ,  $df = 5$ ,  $P \leq .01$ ). In stepwise multiple regression, pH and alkalinity were identified as the principal variables predictive of strontium concentrations (adjusted  $r^2 = .97$ ,  $P \leq .01$ ). Sediment strontium concentrations were also strongly correlated with concentrations of strontium in the water, including total strontium ( $r^2 = .68$ ,  $df = 5$ ,  $P \leq .05$ ) and dissolved strontium ( $r^2 = .85$ ,  $df = 5$ ,  $P \leq .01$ ). There were no significant correlations between other metals and water quality variables.

## Trace Elements in 1988 Study

Trace elements meeting quality control standards in 1988 sediments include arsenic, beryllium, cadmium, chromium, copper, lead, magnesium, manganese, molybdenum, nickel, strontium, thallium, tin, vanadium, and zinc (Table 13). Most cadmium and thallium concentrations were at or below detection. However, the metals occur at a higher concentration at Site 1, the Hogatza River ( $\bar{x}$  = 0.7 mg/kg Cd and 14.3 mg/kg Tl) than at other sites sampled. The remaining metals were present in most samples. Mean trace element concentrations at the sites in mg/kg dry weight were barium, 47 - 165; beryllium, 0.1 - 0.4; chromium, 12.7 - 25.9; copper, 10.9 - 33.2; lead, 7.5 - 16.5; magnesium, 3740 - 6713; manganese, 192 - 538; molybdenum, 0.4 - 1.8; nickel, 14.5 - 30.3; strontium, 13.1 - 49.7; tin, 5.2 - 6.9; vanadium, 20.4 - 42.4; and zinc 34.6 - 81.3.

No significant differences among sites were observed for tin. Significant differences were found in the concentrations of other metals among sites using a one-way analysis of variance (Table 14). Site 3 (Bishop Creek) tended to be lowest in both total divalent cations (Ba, Mg, Mn, and Sr) and in total heavy metals (Be, Cr, Cu, Pb, Mo, V, and Zn) of any site examined. Site 4 (Clear Creek) was also generally low in both divalent cations and heavy metal concentrations in sediments. In contrast, Site 5 (Bonanza Creek) tended to exhibit the highest concentrations of many of divalent cations and heavy metals. Site 6 (Caribou Creek) also appeared slightly enriched in some metals (Be, Cr, Mo, V), and Site 1 (Hogatza River) contained higher concentrations of Be, Cr, and V than other sites. While statistical differences were demonstrated among sites, the absolute differences in metal concentrations among sites were not particularly large.

As in 1987, many metals were highly correlated with each other (Table 15). The metals most highly correlated with each other ( $P \leq .01$ ) included beryllium and chromium ( $r^2 = .83$ ,  $df = 5$ ), chromium and vanadium ( $r^2 = .81$ ,  $df = 5$ ), copper and manganese ( $r^2 = .93$ ,  $df = 5$ ), copper and nickel ( $r^2 = .82$ ,  $df = 5$ ), copper and zinc ( $r^2 = .88$ ,  $df = 5$ ), and zinc and manganese ( $r^2 = .85$ ,  $df = 5$ ). These data indicate strong beryllium-chromium-vanadium and copper-manganese-zinc associations at the sites.

Comparisons of sediment trace element concentrations and water quality parameters revealed few strong relationships. However, mean magnesium was positively correlated ( $P \leq .05$ ) with mean conductivity, alkalinity, hardness, and turbidity at the sites, while mean tin concentrations at the sites were negatively correlated ( $P \leq .05$ ) with all these variables except pH at the sites. Also, mean chromium and copper concentrations at the sites were positively correlated with conductivity. Our measurements were point-in-time measurements comparing only six sites. A more comprehensive study of geochemistry would be needed to better understand interrelationship of water quality and trace element concentrations.

Table 13. Total metal concentrations in sediment from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1988. Concentrations are reported in mg/kg dry weight.<sup>a</sup>

Site	Date	Ba	Be	Cd	Cr	Cu	Pb	Mg	Mn	Mo	Ni	Sr	Sn	Tl	V	Zn
1	6/28/88	126	0.4	<0.5	25.9	23.1	15.9	5790	447	1.5	26.0	19.0	5.2	<10.9	41.7	67
		106	0.5	0.6	23.7	20.5	11.7	5200	372	1.0	23.5	18.0	6.2	12.6	39.2	59
		131	0.4	1.1	28.0	23.0	13.4	6030	474	1.3	26.9	18.0	4.2	19.5	46.3	69
$\bar{x}$	121	0.4	0.7	25.9	22.2	13.7	5673	431	1.3	25.5	18.3	5.2	14.3	42.4	65	
2B	6/28/88	47	0.2	<0.5	16.4	28.5	15.4	6510	528	1.4	29.9	49.7	5.7	11.0	19.8	78
		47	0.2	<0.5	17.5	29.1	16.9	7040	563	1.8	32.0	51.1	6.0	<10.9	21.5	85
		47	0.2	0.8	16.6	28.6	14.7	6590	523	1.9	29.1	48.2	4.6	<10.9	20.0	81
$\bar{x}$	47	0.2	-	16.8	28.7	15.7	6713	538	1.7	30.3	49.7	5.4	-	20.4	81	
3	6/04/88	61	0.1	<0.5	12.5	9.6	8.3	3920	179	0.5	17.7	16.0	6.2	<10.9	22.6	32
		59	0.1	<0.5	11.7	10.6	7.0	3960	199	0.5	17.9	16.6	6.3	<10.9	20.3	34
		73	0.1	<0.5	13.8	12.4	7.3	4420	198	<0.3	18.01	20.0	5.7	<10.9	23.8	38
$\bar{x}$	64	0.1	-	12.7	10.9	7.5	4100	192	0.8	17.9	17.5	6.7	-	22.2	35	
4	6/30/88	138	0.4	0.5	25.7	20.1	14.1	5210	446	0.9	21.1	19.2	8.3	11.6	40.4	58
		108	0.3	<0.5	20.0	15.7	13.4	3790	273	1.8	14.5	14.3	5.0	<10.9	27.3	40
		36	0.2	<0.5	11.5	7.5	7.1	2220	193	1.3	7.9	5.7	6.7	<10.9	20.7	19
$\bar{x}$	94	0.3	-	19.1	14.4	11.5	3740	304	1.3	14.5	13.1	6.7	-	29.5	39	
5	7/02/88	163	0.3	<0.5	23.3	30.4	16.7	4300	701	1.6	30.4	22.1	6.2	<10.9	29.9	80
		163	0.3	0.6	21.8	31.6	15.5	4030	709	2.0	30.3	22.0	6.9	<10.9	27.8	80
		168	0.4	0.8	21.7	37.6	17.3	3830	723	1.9	31.0	26.2	5.3	<10.9	29.7	79
$\bar{x}$	165	0.3	0.7	22.3	33.2	16.5	4053	711	1.8	30.6	23.4	6.1	-	29.1	80	
6	6/30/88	96	0.3	<0.5	21.6	17.7	11.5	4000	253	1.5	16.4	12.7	6.2	<10.9	29.6	42
		114	0.4	0.7	24.3	21.7	13.8	4190	420	1.8	19.2	14.7	7.3	<10.9	34.3	47
		113	0.4	<0.5	25.9	21.2	15.7	4630	369	2.0	20.3	15.1	7.2	<10.9	35.9	49
$\bar{x}$	108	0.4	-	23.9	20.2	13.7	4273	347	1.8	18.6	14.2	6.9	-	33.3	46	

<sup>a</sup> Mean concentrations were computed using  $\frac{1}{2}$  the detection limit for a nondetect if remaining replicate concentrations of an analyte were positive.

Table 14. Results of one-way analysis of variance for sediment metal concentrations by site. Mean concentrations are reported in mg/kg dry weight. Different letters distinguish sites that were significantly different ( $P \leq .05$ ) from each other.

Site	Ba	Be	Cr	Cu	Pb	Mg	Mn	Mo	Ni	Sr	V	Zn
1	121 <sup>a</sup>	0.4 <sup>ab</sup>	25.9 <sup>ab</sup>	22.2 <sup>ac</sup>	13.7 <sup>ab</sup>	5673 <sup>ab</sup>	431 <sup>a</sup>	1.3 <sup>ab</sup>	25.5 <sup>ab</sup>	18.3 <sup>ab</sup>	42.4 <sup>a</sup>	64.9 <sup>ab</sup>
2	47 <sup>b</sup>	0.2 <sup>b</sup>	16.8 <sup>b</sup>	28.7 <sup>ab</sup>	15.7 <sup>b</sup>	6713 <sup>b</sup>	538 <sup>abd</sup>	1.7 <sup>b</sup>	30.3 <sup>a</sup>	49.7 <sup>a</sup>	20.4 <sup>b</sup>	81.3 <sup>a</sup>
3	64 <sup>b</sup>	0.1 <sup>c</sup>	12.7 <sup>c</sup>	10.9 <sup>d</sup>	7.5 <sup>ab</sup>	4100 <sup>a</sup>	192 <sup>c</sup>	0.4 <sup>a</sup>	17.9 <sup>bc</sup>	18.6 <sup>ab</sup>	22.2 <sup>b</sup>	34.6 <sup>c</sup>
4	94 <sup>b</sup>	0.3 <sup>b</sup>	19.1 <sup>b</sup>	14.4 <sup>cd</sup>	11.5 <sup>ab</sup>	3740 <sup>a</sup>	304 <sup>c</sup>	1.3 <sup>b</sup>	14.5 <sup>c</sup>	13.1 <sup>a</sup>	29.5 <sup>ab</sup>	38.9 <sup>bc</sup>
5	165 <sup>ac</sup>	0.3 <sup>b</sup>	22.3 <sup>b</sup>	33.2 <sup>b</sup>	16.5 <sup>b</sup>	4053 <sup>a</sup>	711 <sup>bd</sup>	1.8 <sup>b</sup>	30.6 <sup>a</sup>	23.4 <sup>b</sup>	29.1 <sup>ab</sup>	80.0 <sup>a</sup>
6	108 <sup>b</sup>	0.4 <sup>ab</sup>	23.9 <sup>ab</sup>	20.2 <sup>acd</sup>	13.7 <sup>ab</sup>	4273 <sup>a</sup>	347 <sup>ac</sup>	1.8 <sup>b</sup>	18.6 <sup>bc</sup>	14.2 <sup>ab</sup>	33.3 <sup>ab</sup>	45.8 <sup>bc</sup>

Table 15. Correlation matrix for 1988 sediment metals from six refuge river sites, with three replicates per site. Correlation coefficients (r) are presented for one-tailed tests.

Element	Ba	Be	Cr	Cu	Pb	Mg	Mn	Mo	Ni	Sr	V
Be	.6970**										
Cr	.7694**	.9183**									
Cu	.5135*	.4638*	.4794*								
Pb	.5366*	.5792**	.6563**	.8992**							
Mg	-.1514	.2074	.2670	.4789*	.5106*						
Mn	.5820**	.4271*	.4726*	.9638**	.8623**	.3851					
Mo	.3506	.4417*	.4708*	.6812**	.7907**	.1552	.6391**				
Ni	.3556	.2949	.3541	.9067**	.7746**	.6837**	.8856**	.4118*			
Sr	-.3156	-.1444	-.1526	.5995**	.4948*	.7900**	.5108*	.2690	.7230**		
V	.6660**	.8421**	.8989**	.1518	.3206	.1539	.1728**	.1150	.1101	-.3928*	
Zn	.3766	.3778	.4271*	.9406**	.8495**	.6936**	.9196**	.5364*	.9742**	.7290**	.1475**

\*  $P \leq .05$

\*\*  $P \leq .01$

## Comparison of Trace Elements in Sediments in 1987 and 1988

Concentrations of trace elements reported in sediment in the two years did not differ significantly from each other using paired-t comparisons, indicating general consistency between 1987 and 1988 lab results for analytes passing QC screening both years (copper, lead, molybdenum, nickel, strontium). However, improved detection limits for lead and molybdenum in 1988 resulted in fewer nondetects for these metals. One possible discrepancy between years was for copper at Site 3. The mean concentration reported in 1987, 10.9 mg/kg, was much lower than that observed in 1988, 22.4 mg/kg.

### *Fish*

Fish collected in 1987 (Table 16) included three northern pike from Site 1, five northern pike each from Sites 2, 3, and 5, and three northern pike from Site 6. Also, one longnose sucker, one broad whitefish, and one humpback whitefish were collected from Site 1 and one Arctic grayling was collected from Site 4. Collections in 1988 (Table 17) consisted of three northern pike from Site 1, four northern pike from Sites 3 and 5, and five northern pike from Sites 5 and 6. In addition, three Arctic grayling were obtained from Site 4 and one sheefish was collected at Site 5. Liver, muscle, and kidney were analyzed from all fish in 1987; only muscle and liver tissues were analyzed from fish collected in 1988. One grayling liver and one pike muscle sample in this latter collection were not analyzed.

### Trace Elements in Fish in 1987

Analytes passing quality control screening include antimony, beryllium, barium, cadmium, chromium, lead, manganese, nickel, silver, and tin. Tables 18, 19, and 20 show results of these analyses by tissue and species.

*Trace elements in fish muscle tissue.* Silver, beryllium, cadmium, and vanadium were not detected in any muscle sample. Lead was only detected in one muscle sample, a northern pike from Site 2 at a concentration of 5.16 mg/kg. Barium was also detected from only one fish muscle sample, a northern pike from Site 1 at a concentration of 0.43 mg/kg. Antimony was detected in two fish, a pike from Site 2 (0.112 mg/kg) and an Arctic grayling from Site 4 (0.153 mg/kg). Chromium was present in only four fish, two northern pike from Site 5 (0.43 and 0.64 mg/kg) and two pike from Site 6 (0.54 and 0.58 mg/kg). Nickel was also uncommonly found in the muscle samples. Nickel was observed in two northern pike from Site 2 (6.72 and 6.73 mg/kg) and one pike from Site 5 (3.00 mg/kg).

The only trace elements present in all the fish muscle samples for which acceptable quality control data were available were manganese and tin. One-way analysis of variance of manganese and tin in northern pike muscle did not reveal any significant differences among sites.

Table 16. Fish samples collected from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1987.<sup>a</sup>

Site	Species	Date	Weight (gm)	Total Length (mm)	Fork Length (mm)	Condition Index	Proportion Moisture		
							Muscle	Liver	Kidney
1	NP	6/04/87	3150	800	763	0.718	.73	.72	.83
	NP	6/04/87	1850	675	650	0.674	.79	.74	.84
	NP	6/04/87	408	411	391	0.688	.78	.68	.84
2	NP	6/26/87	680	460	435	0.855	.78	.61	.84
	NP	6/26/87	1150	595	575	0.621	.79	.75	.80
	NP	7/23/87	1300	590	555	0.781	.77	.56	.80
	NP	7/23/87	1443	840	781	0.304	.76	.59	.76
	NP	7/23/87	2800	755	715	0.782	.78	.69	.82
3	NP	6/11/87	870	530	490	0.739	.79	.76	.83
	NP	7/19/87	680	485	460	0.699	.78	.70	.82
	NP	7/19/87	1125	575	545	0.676	.78	.75	.83
	NP	7/19/87	1370	620	595	0.667	.77	.62	.83
	NP	7/19/87	1100	560	535	0.739	.77	.72	.81
5	NP	7/18/87	1575	635	600	0.729	.76	.64	.82
	NP	7/18/87	2080	720	690	0.633	.78	.69	.84
	NP	7/18/87	2750	780	745	0.652	.79	.76	.83
	NP	7/18/87	2475	770	740	0.611	.77	.63	.72
	NP	7/18/87	2810	740	705	0.785	.76	.66	.81
6	NP	8/10/87	1125	562	525	0.756	.76	.68	.80
	NP	8/10/87	860	574	543	0.546	.80	.75	.85
	NP	8/10/87	5220	910	875	0.793	.77	.68	.79
1	LNS	6/04/87	1085	542	513	0.804	.74	.69	.78
	BWF	6/04/87	1580	527	506	1.219	.78	.69	.86
	HWF	6/04/87	1675	553	511	1.255	.73	.68	.76
4	AG	6/06/87	875	444	-	-	.73	.78	.83

<sup>a</sup> NP = northern pike; LNS = longnose sucker; BWF = broad whitefish; AG = Arctic grayling; HWF = humpback whitefish

Table 17. Fish samples collected from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1988.<sup>a</sup>

Site	Species	Date	Weight (gm)	Total Length (mm)	Fork Length (mm)	Condition Index	Proportion Moisture	
							Liver	Muscle
1	NP	6/30/88	2603	742	704	0.746	0.74	0.79
	NP	8/11/88	323	380	355	0.722	0.66	0.78
	NP	8/11/88	438	415	398	0.695	0.69	0.78
	NP	8/11/88	606	462	435	0.736	0.67	0.78
	NP	8/11/88	440	425	405	0.662	0.70	0.78
2	NP	6/28/88	573	465	437	0.687	0.76	0.79
	NP	6/28/88	987	571	544	0.613	0.75	0.80
	NP	6/28/88	701	504	476	0.650	0.77	0.81
	NP	6/28/88	2108	662	632	0.835	0.73	0.79
	NP	6/28/88	902	535	508	0.688	0.68	0.79
3	NP	6/04/88	655	476	416	0.910	0.71	0.78
	NP	6/04/88	1205	615	548	0.732	0.77	0.79
	NP	6/04/88	1157	590	553	0.684	0.75	0.79
	NP	6/04/88	2390	730	690	0.728	0.69	0.78
5	NP	7/02/88	5000	890	820	0.428	0.73	0.78
	NP	7/02/88	1436	735	695	0.481	0.74	0.77
	NP	7/02/88	1383	702	660	0.411	0.72	0.78
	NP	7/02/88	1271	715	676	0.443	0.74	0.73
	NP	7/02/88	1274	705	660	0.939	0.79	0.73
6	NP	6/30/88	833	471	446	0.798	0.70	0.78
	NP	6/30/88	1263	572	541	0.776	0.62	0.79
	NP	8/11/88	1850	650	620	0.774	0.58	0.77
	NP	8/11/88	1324	590	555	0.765	0.60	0.77
	NP	8/11/88	1532	620	585	0.765	0.68	0.78
4	AG	6/30/88	458	366	342	1.145	0.76	0.77
	AG	6/30/88	665	421	391	1.112	0.78	0.79
	AG	6/30/88	620	411	384	1.095	0.76	0.77
	AG	6/30/88	618	415	382	1.109	0.76	0.77
5	SF	7/02/88	5000	890	820	0.907	0.73	0.77

<sup>a</sup> NP = northern pike; AG = Arctic grayling; SF = sheefish

Table 18. Trace elements in fish muscle tissue from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1987. Residues are reported in mg/kg dry weight.<sup>ab</sup>

Site	Species	Sb	Ba	Cr	Mn	Ni	Sn
1	NP	<0.093	1.86	<0.37	1.38	<1.49	7.70
	NP	<0.120	<2.38	<0.48	1.48	<1.90	12.20
	NP	<0.113	<2.24	<0.45	3.23	<1.79	6.59
	$\bar{x}$	-	-	-	2.03	-	8.83
	LNS	<0.098	<1.95	<0.39	3.39	<1.56	11.00
	BWF	<0.115	<2.29	<0.46	1.01	<1.83	9.86
	HWF	<0.094	<1.87	<0.37	0.78	<1.49	7.69
2	NP	<0.114	<2.27	<0.45	1.45	<1.82	12.10
	NP	<0.120	<2.39	<0.48	2.39	<1.91	11.90
	NP	<0.108	<2.20	<0.50	1.98	<1.80	7.54
	NP	0.112	<2.10	<0.50	2.03	6.72	11.40
	NP	<0.113	<2.30	<0.50	1.48	6.73	17.40
$\bar{x}$	-	-	-	1.87	-	12.67	
3	NP	<0.117	<2.40	<0.50	1.12	<1.90	9.53
	NP	<0.115	<2.30	<0.50	2.05	<1.90	11.70
	NP	<0.114	<2.30	<0.50	1.13	<1.90	8.10
	NP	<0.109	<2.20	<0.50	2.81	<1.80	12.10
	NP	<0.111	<2.30	<0.50	0.84	<1.80	11.30
$\bar{x}$	-	-	-	1.59	-	10.55	
4	AG	0.153	<1.90	<0.40	3.61	<1.50	9.05
5	NP	<0.106	<2.20	0.64	1.82	<1.70	7.12
	NP	<0.112	<2.30	<0.50	1.12	<1.80	8.17
	NP	<0.117	<2.40	<0.50	0.88	<1.90	8.98
	NP	<0.108	<2.20	0.43	1.59	3.00	12.70
	NP	<0.105	<2.10	<0.42	1.17	<1.70	12.00
$\bar{x}$	-	-	-	1.32	-	9.79	
6	NP	<0.104	<2.10	0.58	1.37	<1.70	7.76
	NP	<0.124	<2.50	0.54	2.52	<2.00	6.14
	NP	<0.110	<2.20	<0.50	0.87	<1.80	8.34
$\bar{x}$	-	-	0.46	1.45	-	8.81	

<sup>a</sup> NP = northern pike; LNS = longnose sucker; BWF = broad whitefish; HWF = humpback whitefish; and AG = Arctic grayling.

<sup>b</sup> Ag, Be, Cd, and V were analyzed, but were not detected in any muscle sample; Pb was detected once (see text).

Table 19. Trace elements in fish livers from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1987. Residues are reported in mg/kg dry weight.<sup>ab</sup>

Site	Species	Cd	Cr	Mn	Sn
1	NP	<0.18	<0.36	3.49	6.51
	NP	<0.20	<0.39	3.07	6.38
	NP	<0.22	<0.44	3.64	7.23
	$\bar{x}$	-	-	3.40	6.71
2	LNS	0.94	<0.33	36.80	4.33
	BWF	0.25	<0.32	4.87	5.86
	HWF	<0.15	<0.31	8.95	6.69
	NP	<0.18	<0.33	3.55	6.93
	NP	0.44	<0.40	7.50	3.69
	NP	<0.12	<0.30	1.61	5.26
2	NP	<0.13	<0.30	0.85	5.85
	NP	<0.16	<0.32	3.01	6.50
	$\bar{x}$	-	-	3.30	5.65
	3	NP	<0.21	<0.50	4.29
3	NP	<0.17	<0.33	4.79	8.92
	NP	<0.20	<0.40	3.48	9.88
	NP	<0.13	<0.26	2.55	6.30
	NP	<0.18	<0.40	2.63	10.20
	$\bar{x}$	-	-	3.55	8.98
4	AG	<0.23	<0.50	30.70	11.30
5	NP	<0.14	<0.30	2.31	7.50
	NP	<0.16	0.32	4.23	6.25
	NP	<0.21	<0.50	4.39	7.54
	NP	<0.14	<0.30	2.70	7.25
	NP	<0.15	<0.30	2.04	5.39
$\bar{x}$	-	-	3.13	6.79	
6	NP	<0.16	0.40	3.98	5.59
	NP	<0.25	<0.45	9.35	10.10
	NP	<0.16	<0.40	3.11	7.48
$\bar{x}$	<0.18	-	4.32	7.07	

<sup>a</sup> NP = northern pike; LNS = longnose sucker, BWF = broad whitefish; HWF = humpback whitefish; and AG = Arctic grayling.

<sup>b</sup> Be and Pb were not detected in any liver sample; Ag, Ba, Ni, Sb, and V were detected in only one fish each (see text).

Table 20. Trace elements in fish kidneys from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1987. Residues are reported in mg/kg dry weight.<sup>ab</sup>

Site	Species	Sb	Cd	Cr	Mn	Sn
1	NP	<0.148	0.47	<0.59	2.43	3.14
	NP	0.432	<0.31	<0.62	2.41	3.33
	NP		<0.68	<1.30	2.84	8.60
	$\bar{x}$	-	-	-	2.56	5.02
2	LNS		2.14	<0.89	3.21	7.78
	BWF	<0.179	0.64	<0.71	2.93	4.79
	HWF	<0.094	<0.19	<0.37	0.78	7.69
	NP		<0.77	<0.96	3.14	7.50
	NP	0.347	0.51	0.71	8.57	6.84
	NP		<0.31	<0.56	2.93	9.29
	NP	0.231	<0.21	<0.50	2.69	8.84
	NP	0.220	<0.28	<0.60	2.47	11.40
	$\bar{x}$	0.266	-	-	3.96	8.77
3	NP		<0.29	<0.60	2.18	10.20
	NP		<0.44	<0.93	2.62	12.50
	NP		0.34	<0.60	2.11	11.40
	NP	0.196	0.77	<0.66	3.39	8.81
	NP	0.151	0.43	<0.60	1.77	10.50
	$\bar{x}$	0.173	0.38	-	2.41	10.68
4	AG	<0.145	<0.29	<0.60	7.05	11.00
5	NP	0.483	<0.28	<0.60	2.33	11.40
	NP	0.589	0.32	<0.70	3.35	11.10
	NP	0.600	<0.30	0.82	2.29	9.18
	NP	8.000	<0.43	0.86	1.94	11.90
	NP	0.435	<0.26	0.57	3.52	10.90
	$\bar{x}$	3.369	-	-	2.69	10.90
6	NP	<0.127	<0.26	0.56	2.94	10.50
	NP		0.80	<0.70	3.67	9.67
	NP	<0.216	<0.24	0.89	1.69	10.90
	$\bar{x}$	-	-	0.58	2.75	10.49

<sup>a</sup> NP = northern pike; LNS = longnose sucker, BWF = broad whitefish; HWF = humpback whitefish; and AG = Arctic grayling.

<sup>b</sup> Ni was not detected; Ba, Ag, and V were detected in only one fish each (see text).

*Trace elements in fish liver tissue.* Beryllium and lead were analyzed, but were not detected in any liver sample. Barium was detected in only one liver sample, that of a longnose sucker from Site 1 (2.08 mg/kg). This fish also contained the only detectable vanadium concentration in any liver (1.63 mg/kg). Similarly, nickel was only detected in one liver sample, from a northern pike from Site 2 at a concentration of 1.00 mg/kg. Silver was detected in one northern pike liver from Site 3 (1.61 mg/kg). Antimony was found in one northern pike liver from Site 3 at a concentration of 0.105 mg/kg.

Cadmium occurred in only three fish liver samples, including those from two Site 1 fish, a longnose sucker (0.94 mg/kg) and a broad whitefish (0.25 mg/kg), and from one northern pike from Site 2 (0.44 mg/kg). Chromium occurred in two northern pike livers, one from Site 5 (0.32 mg/kg) and one from Site 6 (0.40 mg/kg). The only trace elements that met quality control criteria and were found consistently in all fish livers were manganese and tin. One-way analysis of variance of these metals in livers of northern pike did not reveal any significant difference among sites in liver manganese concentrations. Differences among sites were significant for tin ( $F_{4,16} = 3.97$ ,  $P \leq .05$ ), with Site 3 (Bishop Creek) exhibiting significantly higher liver tin concentrations ( $\bar{x} = 8.98$  mg/kg) than Site 2, with the lowest reported concentrations of tin ( $\bar{x} = 5.65$  mg/kg). However, one-way Kruskal-Wallis analysis of variance failed to confirm significant differences among sites ( $\chi^2 = 7.89$ ,  $P = .0957$ ).

*Trace elements in fish kidney tissue.* Nickel was analyzed, but was not detected in any fish kidney sample. Barium was detected in only one northern pike kidney from Site 1 (6.48 mg/kg). Silver was also detected in only one northern pike kidney, from Site 3 (3 mg/kg); this was the same fish that exhibited detectable silver in its liver. The single Arctic grayling kidney from Site 4 contained the only vanadium (14.4 mg/kg).

Cadmium was detected sporadically in fish kidneys, which are known to concentrate this metal. The highest concentration was in a longnose sucker from Site 1 (2.14 mg/kg). The remaining fish contained  $< 1$  mg/kg. Another metal that was present sporadically was chromium. Chromium was not detected in kidney samples from Sites 1, 3, or 4 (one grayling only), but was found in one pike from site 2 (0.71 mg/kg), three of six pike from Site 5, Bonanza Creek (0.57 - 0.82 mg/kg), and in two of three pike from Site 6, Caribou Creek (0.56 - 0.89 mg/kg).

The only trace elements that met quality control criteria and were found in most or all fish kidneys were antimony, manganese, and tin. Antimony was detected in the kidneys of 11 of the northern pike analyzed (7 pike were not analyzed for antimony). The antimony occurred in kidney samples at every site with northern pike except Site 6 (Caribou Creek). By far, the highest concentration was from a northern pike at Site 5, Bonanza Creek (8.00 mg/kg). All other fish contained less than 1 mg/kg in the kidney.

One-way analysis of variance of these metals in kidneys of northern pike revealed no significant differences among sites in pike kidney concentrations of antimony or manganese,

but significant differences for tin ( $F_{4,16} = 7.35$ ,  $P \leq .01$ ). In contrast, Kruskal-Wallis one-way analysis of variance showed significant differences among sites for both antimony ( $\chi^2 = 10.77$ ,  $n = 14$ ,  $P = .029$ ) and tin ( $\chi^2 = 9.95$ ,  $n = 21$ ,  $P = .041$ ). For antimony, Site 5 (Bonanza Creek) fish kidneys ranked the highest in antimony levels, and Site 6 (Caribou Creek) fish kidneys ranked the lowest.

For tin, kidneys from Sites 3 (Bishop Creek), 5 (Bonanza Creek), and 6 (Caribou Creek) all showed significantly higher concentrations ( $> 10$  mg/kg) than those from Site 1 (Hogatza River) with the lowest concentration in pike kidneys (5 mg/kg). None of these sites differed significantly ( $P \leq .05$ ) from Site 2, the Koyukuk River (8.8 mg/kg). Kruskal-Wallis rankings were similar to those in the parametric procedure.

*Relationship of trace metal concentrations in different fish tissues.* The concentrations of manganese differed significantly among tissues ( $F_{2,60} = 10.74$ ,  $P \leq .01$ ). Northern pike livers ( $\bar{x} = 3.65$  mg/kg) and kidneys ( $\bar{x} = 2.91$  mg/kg) contained significantly higher concentrations of manganese than did muscle samples ( $\bar{x} = 1.65$  mg/kg). Significant differences in tin distribution among these tissues are also apparent ( $F_{2,60} = 8.55$ ,  $P \leq .01$ ). However, tin was concentrated in muscle ( $\bar{x} = 10.04$  mg/kg) and liver ( $\bar{x} = 9.42$  mg/kg) tissues, rather than kidneys ( $\bar{x} = 7.16$  mg/kg). The other notable difference in tissue distribution was in antimony, present in 1 pike muscle sample, no pike livers, and in 11 of 17 northern pike kidneys analyzed for antimony. A similar pattern was observed for cadmium, which was not detected in pike muscle samples, detected in only 2 pike livers, and found in 6 of 21 pike kidneys. The sporadic presence of cadmium and chromium in muscle or liver tissue did not reliably predict concentrations in the kidney.

*Correlations of trace metal concentrations in fish, water, and sediments.* The only significant differences in fish metal concentrations found among sites was in the distribution of tin in fish livers and kidneys. None of the tin data for either water or sediment samples was acceptable, so no correlations were possible between tissue concentrations and those in water or sediment. Correlations were performed to assess the relation of tissue tin concentrations and water quality parameters. No significant relationships were observed.

*Relationship of trace metal concentrations, fish condition, and site.* The relationships between fish metrics for northern pike, including weight, fork length, total length, and condition factor (K) and manganese and tin in liver and muscle samples and antimony, manganese, and tin in kidney samples were explored through the use of scatterplots and through one-way analysis of variance and correlation analysis. Weight, length, and condition factor of northern pike did not differ significantly among sites. As expected, total length, fork length, and weight of the fish were all positively correlated with each other ( $P \leq .01$ ). Manganese concentrations in muscle, liver, and kidney were all negatively correlated with the length, weight, and condition index of northern pike. However, the only significant relationships were negative correlations between muscle manganese and these fish metrics.

The strongest relationship observed was between muscle manganese concentrations and pike weight ( $r^2 = .26$ ,  $df = 20$ ,  $P \leq .05$ ). This relationship appears weak at best (Figure 4).

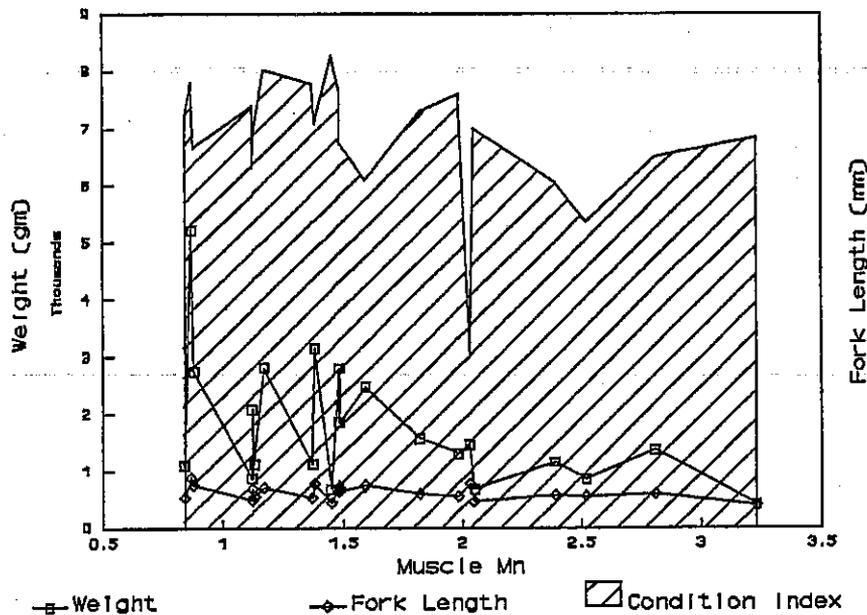


Figure 4. Relationship between manganese concentrations in northern pike muscle, weight, fork length, and fish condition in 1987.

No significant relationships were observed between muscle, liver, or kidney tin concentrations and northern pike lengths, weight, or condition index, nor were any significant relationships observed between kidney antimony concentrations and these variables.

#### Trace Elements in Fish in 1988

Trace elements meeting quality control criteria in tissues analyzed in 1988 include arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, magnesium, manganese, molybdenum, nickel, selenium, strontium, thallium, vanadium, and zinc. Mercury failed to meet quality control criteria for tissues, despite relatively high concentrations of mercury reported in some pike muscle and liver samples. Quality control data suggest that mercury was present in certain fish at high concentrations, but that the concentrations cannot be reliably quantified from existing data. For the same reasons, aluminum, antimony, and silver data are questionable and are omitted from presentation.

*Trace elements in fish muscle tissue.* Arsenic, beryllium, cadmium, and lead were below detection limits for all muscle samples. Boron and thallium were present in reportable concentrations in only one fish sample each. Boron was present in the muscle tissue of a northern pike from Site 2 at a concentration of 0.46 mg/kg, a concentration slightly below the detection limit for most other samples. Thallium was detected in a pike from Site 1, again at a concentration (14 mg/kg) approximating the detection limit. Other trace elements present in the fish are shown in Table 21.

Trace elements present in most or all northern pike muscle samples included barium, copper, iron, magnesium, manganese, strontium, and zinc. No significant differences among sites were identified for the concentrations of barium, copper, iron, magnesium, and zinc in northern pike muscle samples using one-way analysis of variance. Significant differences among sites were observed in muscle manganese concentrations ( $F_{4,17} = 4.096$ ,  $P \leq .05$ ), with Site 5 (Bonanza Creek) fish containing significantly higher concentrations of manganese ( $\bar{x} = 5.96$  mg/kg) than fish at the other four sites with northern pike (Site 4 lacked northern pike). Similarly, significant differences occurred among sites in muscle strontium of pike ( $F_{4,17} = 3.350$ ,  $P \leq .05$ ); however, the Scheffe procedure did not discriminate among sites, indicating that differences in strontium were not great.

Kruskal-Wallis one-way analysis of variance of the same data identified more significant differences among sites, including differences in northern pike muscle concentrations of barium ( $\chi^2 = 9.826$ ,  $n = 21$ ,  $P \leq .05$ ); copper ( $\chi^2 = 11.644$ ,  $n = 21$ ,  $P \leq .05$ ); iron ( $\chi^2 = 12.606$ ,  $n = 21$ ,  $P \leq .05$ ); manganese ( $\chi^2 = 11.628$ ,  $n = 21$ ,  $P \leq .05$ ); and zinc ( $\chi^2 = 12.496$ ,  $n = 21$ ,  $P \leq .05$ ). In these analyses, Site 1 (Hogatza River) ranked highest in barium and manganese concentrations in the muscle samples; Site 2 (Koyukuk River) ranked highest in magnesium concentration; and Site 5 fish ranked highest in copper, iron, and zinc concentrations. Site 3 (Bishop Creek) ranked lowest in the concentrations of all muscle trace elements. The lack of correspondence between parametric and nonparametric results for some of these metals indicates that distributions of these trace elements deviated sufficiently from normality and/or homogeneity of variance that the latter results are more applicable than the former results.

*Trace elements in fish liver tissue.* Beryllium and strontium were below the detection limit in all pike liver samples. Arsenic, lead, and thallium were detected in liver tissue from only one fish each. Arsenic was detected in a northern pike from Site 2 (0.87 mg/kg). Lead was present in a pike liver from Site 6 at a concentration of 3.2 mg/kg, very near the detection limit, and thallium was found in an Arctic grayling liver from Site 4 at a concentration of 13.8 mg/kg, also very near the detection limit. Nickel was also uncommonly detected. It occurred at concentrations of 0.96 and 1.20 mg/kg in two northern pike livers and at a concentration of 1.50 mg/kg in a sheefish liver. Boron was detected in only 4 of 23 northern pike (0.49 - 1.80 mg/kg), but in all 3 grayling livers analyzed (1.20 - 2.90 mg/kg), suggesting that grayling may bioaccumulate this metalloids more effectively than northern pike. Other trace elements present in fish livers are presented in Table 22.

Table 21. Trace elements in fish muscle tissue from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1988. Residues are reported in mg/kg dry weight.<sup>ab</sup>

Site	Species	Ba	Cr	Cu	Fe	Mg	Mn	Mo	Ni	Se	Sr	V	Zn
1	NP	0.31	0.31	1.0	9	1250	1.9	<0.30	<0.99	.53	2.5	<0.30	16.7
	NP	0.43	0.49	0.8	24	1340	4.1	<0.30	<1.00	.86	3.2	<0.30	23.2
	NP	0.68	0.61	0.7	30	1330	5.2	<0.30	<1.00	1.10	4.7	0.30	30.9
	NP	0.86	<0.30	0.7	19	1430	10.5	<0.30	<0.99	1.40	6.8	<0.30	29.3
	NP	0.70	<0.30	1.2	38	1460	8.1	<0.30	<8.00	1.10	4.8	<0.30	29.2
	$\bar{x}$	0.60	-	0.9	24	1362	6.0	-	-	1.00	4.4	-	25.9
2	NP	0.29	<0.30	0.7	12	1480	2.9	<0.30	<0.99	1.00	3.5	<0.30	15.5
	NP	0.28	<0.30	1.7	9	1410	3.7	<0.30	3.00	.96	3.7	<0.30	19.2
	NP	0.27	<0.30	1.1	13	1360	2.6	<0.30	<0.99	1.00	1.6	<0.30	18.0
	NP	0.23	<0.26	0.4	5	1370	1.6	<0.26	<0.88	1.30	1.8	<0.26	12.4
	NP	0.28	<0.30	1.9	15	1340	2.7	<0.30	<0.99	1.60	3.9	<0.30	18.4
	$\bar{x}$	0.27	-	1.2	11	1392	2.7	-	-	1.11	2.9	-	16.7
3	NP	0.12	<0.30	1.1	8	1290	1.6	<0.30	<1.00	<0.49	<1.5	<0.30	14.4
	NP	0.21	<0.29	0.7	11	1260	1.0	<0.29	<0.98	0.75	<1.5	<0.29	14.4
	NP	0.23	<0.29	0.5	8	1290	0.9	0.41	<0.97	0.76	2.0	<0.29	13.7
	NP	0.16	<0.30	0.6	6	1310	0.9	<0.30	<0.99	<0.50	1.8	<0.30	14.7
	$\bar{x}$	0.18	-	0.7	8	1288	1.1	-	-	-	-	-	14.3
4	AG	0.65	<0.29	1.8	21	1120	1.8	<0.29	<0.98	1.50	4.7	<0.29	13.8
	AG	0.12	<2.00	2.5	40	1180	1.2	<0.30	<1.00	1.80	<1.5	<0.30	10.9
	AG	0.25	<0.29	1.6	23	1130	1.1	0.33	<0.96	1.60	<1.4	<0.29	14.2
	AG	<0.10	<0.30	2.0	33	1030	1.2	<0.30	<0.99	2.30	<1.5	<0.30	15.5
	$\bar{x}$	0.28	-	1.7	29	1115	1.3	-	-	1.80	-	-	13.6
5	SF	<0.10	<0.30	0.9	23	1210	0.9	<0.30	<1.00	1.00	2.8	<0.30	13.3
	NP	0.24	<0.30	1.9	31	1290	2.3	<0.30	2.00	0.80	<1.5	<0.30	23.0
	NP	1.10	<0.29	1.8	52	1340	4.8	<0.29	<0.97	0.83	3.6	<0.29	21.7
	NP	0.16	0.36	23.5	386	480	4.6	0.45	<1.10	<0.52	<1.6	0.40	111.0
	$\bar{x}$	0.56	-	8.4	146	607	3.1	-	-	0.63	-	-	44.2
6	NP	0.15	0.49	1.3	7	1300	1.0	<0.29	<0.97	1.50	<1.5	<0.29	17.4
	NP	0.35	1.40	41.9	18	1230	1.4	<0.29	17.70	2.30	2.1	<0.29	39.0
	NP	0.75	0.78	2.5	48	1360	3.4	<0.30	<1.00	2.00	3.2	<0.30	17.7
	NP	0.87	0.86	4.3	39	1356	4.9	<0.30	3.70	1.60	4.8	<0.30	19.9
	NP	0.53	0.38	0.9	24	1300	2.6	<0.30	<0.99	1.50	3.3	<0.30	16.8
	$\bar{x}$	0.53	0.86	10.2	27	1309	2.7	-	-	3.00	2.8	-	23.4

<sup>a</sup> NP = northern pike, AG = Arctic grayling, and SF = sheefish

<sup>b</sup> As, Be, Cd, and Pb were analyzed, but were not detected in any muscle tissue; B and Tl were detected in only one fish (see text).

Table 22. Trace elements in fish livers from Koyukuk National Wildlife Refuge and the Northern Unit of Innoko National Wildlife Refuge, 1988. Residues are reported in mg/kg dry weight.<sup>ab</sup>

Site	Species	Ba	B	Cd	Cr	Cu	Fe	Mg	Mn	Mo	Se	V	Zn
1	NP	0.11	0.66	0.51	0.67	23.1	345	380	2.1	<0.30	5.1	0.37	94.8
	NP	0.17	<0.59	<0.59	0.45	9.6	241	438	3.2	<0.36		0.40	103.0
	NP	<0.08	<0.42	0.50	0.34	17.9	516	414	3.6	0.52		<0.25	96.2
	$\bar{x}$	0.11	-	0.44	0.49	16.9	367	411	3.0	-	-	0.30	98.0
2	NP	<0.19	1.80	<0.94	0.66	13.3	495	659	6.7	<0.56		<0.56	144.0
	NP	0.16	<0.50	1.00	1.20	39.6	1150	557	8.4	0.99	5.4	<0.30	265.0
	NP	0.16	<0.49	1.30	0.76	13.2	587	608	7.8	0.77	5.2	0.57	142.0
	NP	0.11	<0.48	0.55	0.45	9.1	137	416	2.7	<0.29	4.9	<0.29	111.0
	NP	<0.10	<0.50	0.74	0.52	20.9	916	353	2.8	0.45	4.4	<0.30	156.0
$\bar{x}$	-	-	0.81	0.73	20.7	657	519	5.7	-	5.0	-	163.6	
3	NP	0.14	<0.50	0.57	0.63	15.1	739	470	3.4	0.78		0.46	156.0
	NP	0.20	<0.47	0.53	2.10	20.9	342	524	5.5	<0.28	3.4	0.44	148.0
	NP	<0.10	<0.50	<0.50	0.34	14.1	212	506	4.3	0.48	3.9	<0.30	135.0
	NP	<0.10	<0.50	<0.50	<0.30	5.3	150	332	1.1	<0.30	3.4	<0.30	60.5
$\bar{x}$	-	-	-	0.81	13.9	361	458	3.6	-	3.6	-	124.9	
4	AG	<0.23	1.20	<1.10	<0.68	27.3	309	703	8.1	<0.68		<0.68	87.1
	AG	0.17	2.90	0.96	0.85	7.8	319	699	10.8	0.84		1.90	87.6
	AG	0.29	2.00	<0.80	0.71	9.2	267	630	7.4	<0.48		0.83	94.0
	$\bar{x}$	0.19	2.03	-	0.63	14.8	298	677	8.8	-	-	1.02	89.6
5	SF	0.75	<0.53	0.75	<0.32	123.0	352	473	9.5	0.78	6.3	0.58	96.4
	NP	<0.10	<0.49	<0.49	0.67	45.8	553	511	6.2	0.59		0.49	217.0
	NP	<0.10	<0.50	<0.50	<0.30	31.2	532	473	9.1	<0.30	5.3	0.82	135.0
	NP	0.15	<0.50	<0.50	<0.30	22.3	338	479	6.0	0.97	6.4	0.68	129.0
	NP	0.46	<0.50	<0.50	0.48	0.7	23	1290	2.5	<0.30	1.0	<0.30	15.6
$\bar{x}$	-	-	-	-	44.6	360	645	6.7	-	4.7	-	118.6	
6	NP	0.16	0.49	<0.49	0.36	12.2	541	431	3.3	0.45		<0.29	86.9
	NP	0.12	<0.50	<0.50	0.32	26.9	1290	354	2.3	0.36	4.2	0.44	61.3
	NP	<0.10	0.86	<0.49	0.43	2.0	1110	341	2.2	0.52	5.0	0.73	71.2
	NP	0.11	<0.49	<0.49	<0.29	15.5	801	287	1.3	<0.29	3.6	<0.29	52.0
	NP	<0.10	<0.48	<0.48	<0.29	29.9	842	411	4.1	<0.29	4.5	0.82	73.3
$\bar{x}$	-	-	-	-	17.3	917	365	2.6	-	4.3	-	65.5	

<sup>a</sup> NP = northern pike, AG = Arctic grayling, and SF = sheefish.

<sup>b</sup> Be and Sr were not detected in any liver tissue; As, Pb, and Tl were detected in only one fish each and Ni was only observed in three fish (see text).

No significant differences among sites were discerned in liver barium, chromium, copper, magnesium, manganese, or zinc concentrations using one-way analysis of variance, and these

results were largely mirrored using Kruskal-Wallis nonparametric comparisons. For iron, significant among-site differences were observed using one-way analysis ( $F_{4,16} = 3.225$ ,  $P \leq .05$ ), but specific differences among sites were not identified using Scheffe multiple range comparisons; nor were significant differences among sites shown in liver iron concentrations using Kruskal-Wallis one-way analysis of variance. For zinc, marginally significant differences among sites were identified in the pike livers ( $\chi^2 = 9.42$ ,  $n = 21$ ,  $P = .051$ ) using the Kruskal-Wallis test. Mean zinc concentrations in northern pike livers ranged from a low concentration of 4.8 mg/kg (Site 6, Caribou Creek) to a high concentration of 16.3 mg/kg (Site 2, Koyukuk River).

*Correlations of metal concentrations in fish, water, and sediments.* The relationships of fish tissue metal residues, water quality, and the same metal residues in water and sediment were explored through correlation analysis. Mean site concentrations of those tissue metals showing significant differences among sites (liver and muscle iron; muscle barium, copper, manganese, strontium and zinc; and liver zinc) were compared with mean site water quality values and mean metal residues in water and sediment at the sites, if these data met quality assurance criteria. Tissue iron concentrations were not significantly correlated with concentrations of total or dissolved iron in the water at the sites or with any average water quality at the site. However, muscle barium concentrations were negatively correlated with pH ( $r^2 = .88$ ,  $df = 5$ ,  $P = .01$ ) and positively correlated with mean concentrations of barium in site sediment ( $r^2 = .72$ ,  $df = 5$ ,  $P = .01$ ). When average pH and sediment barium concentrations were regressed against mean muscle barium at the sites, pH alone predicted muscle barium concentrations; sediment barium did not significantly enhance predictions. Muscle strontium concentrations were positively correlated with only one water quality parameter, turbidity ( $r^2 = .68$ ,  $df = 5$ ,  $P \leq .05$ ), and not to sediment strontium concentrations. Concentration of other trace elements in muscle tissue at the sites were not correlated with any water quality variable nor to the sediment concentration of the same metal.

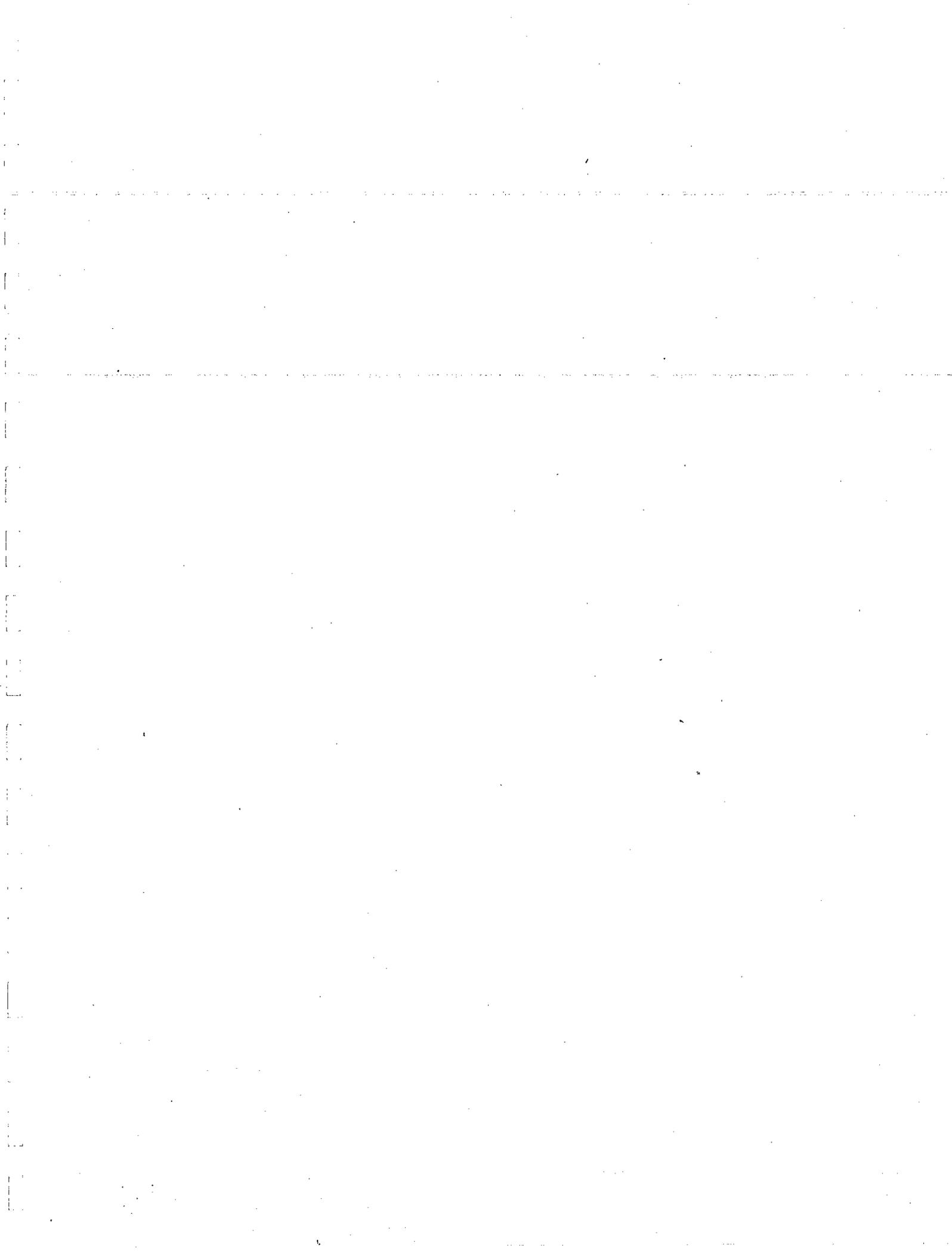
Trace elements in liver tissues were not correlated with the respective metal in sediments. However, zinc concentrations in liver were positively correlated with conductivity ( $r^2 = .88$ ,  $df = 5$ ,  $P \leq .01$ ), alkalinity ( $r^2 = .93$ ,  $df = 5$ ,  $P \leq .01$ ), and hardness ( $r^2 = .91$ ,  $df = 5$ ,  $P \leq .01$ ). Forward stepwise regression suggested that all three variables contribute to this relationship. However, the sample size in the above correlations and regressions was too small to draw any firm conclusions. Additional data will need to be collected to test the correlations observed.

*Relationship of trace metal concentrations, fish condition, and sites.* The relationship of fish metrics and tissue metal concentrations for northern pike, including weight, fork length, total length, and condition factor (K) was examined through the use of analysis of variance, scatterplots, linear correlation, and multiple regression. One-way analysis of variance (including Kruskal-Wallis tests) did not reveal any significant differences in the length, weight, or condition index of northern pike among sites. Scatterplots also did not suggest any clear cases where metal deficiency or metal surpluses resulted in poor growth or condition at the lowest or highest concentrations of trace elements, respectively.

When the relationship of trace elements to fish metrics was explored through correlation analysis, disregarding collection site, several significant relationships between trace element concentration and fish metrics were observed. Muscle magnesium concentration was negatively correlated with total length ( $r^2 = .18$ ,  $df = 22$ ,  $P \leq .05$ ) and fork length ( $r^2 = .17$ ,  $df = 22$ ,  $P \leq .05$ ), and positively correlated with fish condition index ( $r^2 = .30$ ,  $df = 22$ ,  $P \leq .01$ ). Muscle barium ( $r^2 = .19$ ,  $df = 22$ ,  $P \leq .05$ ), copper ( $r^2 = .14$ ,  $df = 22$ ,  $P \leq .05$ ), and manganese ( $r^2 = .17$ ,  $df = 22$ ,  $P \leq .05$ ) were also positively correlated with fish condition index. Muscle strontium was positively correlated with fish condition ( $r^2 = .19$ ,  $df = 22$ ,  $P \leq .05$ ). Most of these relationships are weak and are probably related to the strong positive correlations exhibited among trace elements themselves. For example, muscle barium and manganese were highly correlated ( $r^2 = .99$ ,  $df = 22$ ,  $P \leq .01$ ), as were muscle manganese and copper ( $r^2 = .82$ ,  $df = 22$ ,  $P \leq .01$ ).

Among the trace elements present in liver, barium was positively correlated with fish weight ( $r^2 = .17$ ,  $df = 22$ ,  $P \leq .05$ ), total length ( $r^2 = .24$ ,  $df = 22$ ,  $P \leq .01$ ), and fork length ( $r^2 = .23$ ,  $df = 22$ ,  $P \leq .01$ ), but was not correlated with fish condition. Similar results were observed for chromium, copper, and manganese. In contrast, liver magnesium was negatively correlated with total length ( $r^2 = .15$ ,  $df = 22$ ,  $P \leq .05$ ), fork length ( $r^2 = .13$ ,  $df = 22$ ,  $P \leq .05$ ), and condition index ( $r^2 = .14$ ,  $df = 22$ ,  $P \leq .05$ ).

Correlation analyses (above) revealed very weak relationships between trace elements and fish metrics. Forward stepwise multiple regression analysis was employed to see if trace elements that were significantly correlated to a given metric would, in combination, better predict fish weight, length, or condition index. Muscle magnesium alone best predicted fish condition. No other trace element added to predictive capability. Similarly, liver copper best predicted fork length and total length. None of the trace elements met default criteria for entry into an equation to predict fish weight. Since only a small fraction of the variance is attributable to trace element concentrations examined in this study, other factors are more important in controlling fish growth and condition at the sites.



## Discussion and Conclusions

This study was performed to evaluate potential impacts from off-refuge placer and hard rock mining on refuge fish and riverine habitat and to obtain baseline data on unmined and historically mined drainages in the event of future mining activity. Unfortunately, except for the limited data on water obtained from several rivers sampled in 1986, virtually all of the drainages examined had experienced upstream or historical mining. Therefore, data for a valid unmined reference stream for comparison with 1987 and 1988 data was not available. Another limitation of this study is that no active mining was occurring at any of the previously mined sites proximal to study sites. In fact, the only significant placer mining activity in the area during this study was more than 150 km upstream on tributaries of the Koyukuk River study sites in the Coldfoot/Wiseman area. West (1982) reported that from 29 to 86 percent of 14 metals detected above the mine sites on 11 streams increased below mine sites, including inactive mine sites, indicating the potential to detect some level of impact from inactive mines. However, much greater impacts could potentially be observed below active mine sites. West and Deschu (1984) observed metal concentrations in actively mined stream waters to increase 10 to 10,000 times below the mine site.

The choice of study site locations on the mined streams has also restricted our ability to draw conclusions regarding the impacts of mining at some of the sites. Data for samples collected at the mouth of Caribou Creek provide an estimate of mining impacts to the Hogatza River from mining activities on Bear Creek and Dry Creek, but the data from this sample site do not afford an estimate of impacts on Bear Creek or Dry Creek themselves. Both these drainages have been highly disrupted as a result of mining and no longer flow as continuous streams due to tailings piles in the drainage channels. The intermittent nature of these streams has probably altered fish access and use patterns, eliminating fish from disturbed portions and reducing flows from the mined tributaries into Caribou Creek.

Similarly, the choice of the Bonanza Creek site, about 48 km and several lakes downstream of mining on Camp Creek, and the selection of the Bishop Creek sample location approximately 25 km downstream of mining, also minimize information on contamination that may be occurring on portions of these drainages within the refuge and immediately downstream from mining activity. These sites were selected mainly due to accessibility by float plane and proximity to other refuge study sites, but are only useful in providing baseline for assessing long-distance impacts of mining. Helicopter access should be considered in future studies to access and evaluate upstream locations closer to actual mine sites. Despite these limitations, results of the 1986 - 1988 studies provide valuable reference data in the event of renewed mining activity on these drainages, particularly in the vicinity of sample locations, and provide some information on possible long-term impacts of mining to major anadromous fish drainages.

In terms of water quality, including pH, conductivity, alkalinity, hardness, and settleable solids, streams and rivers sampled in the Koyukuk and Northern Unit of Innoko Refuges resemble many other nonglacial interior Alaska streams -- near neutral in pH, soft to moderate in hardness, and low to average in alkalinity. Waters are typical of calcium-magnesium bicarbonate systems. Potential acidification of surface waters, which may result from the oxidation of iron sulfide ores present near some mine sites (Clarke 1974), was not observed.

All sites except the Hogatza River and the Koyukuk River had low turbidities for rivers, less than 15 NTU in 1987. The Hogatza River was 32.7 NTU and the Koyukuk River was 63.7 NTU. Settleable solids were also measured in Koyukuk River water and in Caribou Creek, and comparatively high suspended solids were measured in the Hogatza River (28 mg/L), Koyukuk River (107 mg/L), and Caribou Creek (63 mg/L). Erosion of mine sites in the Caribou Creek drainage may account for some of the suspended solids in the Hogatza River drainage. However, Caribou Creek's turbidity was only slightly elevated and Clear Creek was very low in turbidity, indicating that the source of turbidity on the Hogatza River was being derived from other sources at the time of sampling, and not directly from these formerly mined streams. The comparatively high turbidity of these rivers in 1987 was not observed in 1988, when all sites were below 10 NTU in turbidity and contained only a trace to nondetectable settleable solids. The lower 1988 turbidities suggests that the higher turbidity is not necessarily characteristic of these sites and may occur episodically, following flood events. Additional time series measurements of these variables are needed to understand sediment loading and its impacts on the drainages.

With a few notable exceptions, surface waters examined in this study were relatively uncontaminated by metals. Molybdenum, thallium, selenium, silver, and tin were either not detected or detected rarely at trace concentrations in total metals samples collected throughout the study. Excluding one anomalous sample from the Koyukuk River in 1986, only low concentrations of antimony, arsenic, beryllium, chromium, nickel, strontium, and zinc were found at the sites in relation to State/Federal water quality criteria.

Cadmium was also not detected, or found in only trace concentrations, in 1986 and 1988. The higher concentrations of cadmium observed in 1987 total metals analyses are inconsistent with 1986 and 1988 observations, and appear to indicate a systematic laboratory error. Similarly, lead was not generally detected in 1986 and occurred at low or nondetectable concentrations in 1988. Therefore, reportable concentrations of lead in 1987, an order of magnitude higher than those reported in 1986 and 1988, are considered suspect. Additional analyses of these metals using atomic absorption spectrometry with a lower detection limit may help resolve these differences.

Vanadium concentrations in refuge surface waters, observed only in 1986 in single grab samples, appear elevated ( $> 0.01$  mg/L) at the Hogatza River, Bishop Creek, and the Gisasa River. However, vanadium was not detected in most 1987 samples, probably due to the higher detection limit employed (0.02 mg/L). Further assessment of vanadium concentrations

therefore appears warranted since vanadium is a toxic metal and three of the concentrations reported in the 1986 study are unusually high for river water.

Several trace elements were present at refuge sites at elevated concentrations. High aluminum concentrations were found in surface water, particularly in the Hogatza River ( $\bar{x}$  = 0.364 mg/L total aluminum and 0.129 mg/kg dissolved aluminum). Concentrations here, as well as in two tributaries to the Hogatza River, Caribou Creek and Clear Creek, are also high in comparison to rivers worldwide, reported to range between 0.030 and 0.064 mg/L (Forstner and Wittmann 1983, Salomons and Forstner 1984). Low pH (usually < 5.6) and high aluminum, either singly or in combination, can result in both acute and chronic toxicity to fish (Cleveland et al. 1986, 1989; Dietrich and Schlatter 1989; McKee et al. 1989). Low pH/high aluminum conditions, in the concentration range observed in this study, are currently believed to be responsible for losses of fishery resources in numerous lakes in the northeastern United States (Haines and Baker 1986, Pauwels and Haines 1986). However, detrimental effects on salmonid species usually require pH concentrations lower than those observed at these sites at the time of measurement (Hunn et al. 1985, Jagoe and Haines 1987, Cleveland et al. 1989). Many factors affect toxicity, including individual sensitivities of fish present and form of aluminum present. Monomeric aluminum, which is not always present and which was not measured in this study, is chiefly responsible for aluminum toxicity (Parkhurst et al. 1990). Also, low temperatures may enhance aluminum toxicity (Villega and Leino 1991), whereas dissolved organic carbon (LaCroix et al., 1990, Parkhurst et al. 1990) and fluoride (Wilkinson et al. 1990) may lower toxicity. Therefore, no conclusions can be drawn based on the studies to date.

The relatively low alkalinity and hardness of the Hogatza watershed suggest poor buffering capacity and susceptibility to acidification events in this area. Spring breakup from snowmelt, acid rain [not frequently observed in interior Alaska], or introduction of organic acids from peats into the drainages as a result of mining could effect additional pH changes, resulting in increased acidity and greater release of cadmium, iron, lead, manganese, mercury, and zinc, in addition to aluminum, into the watershed (Haines 1981, Salomons and Forstner 1984, Wiener 1987, Wiener and Stokes 1990). Future monitoring of alkalinity, pH, and metals is therefore warranted in this watershed. Additional unmined streams in the area also need to be studied to provide reference data for assessing mining effects.

Other metals that were elevated in refuge waters are iron, manganese, copper, and nickel. Iron was elevated on the Hogatza, Koyukuk, Huslia, and Dulbi rivers, and as well as Bishop and Bonanza Creeks. Concentrations often approached or violated the State drinking water quality standard for iron (1 mg/L) during one or more sample periods. The State criterion for manganese (0.05 mg/L) was also exceeded on the Hogatza River in 1987. These conditions are not unusual for interior or northern Alaska drainages, where high iron and manganese also predominate in soils and sediments. However, the iron and manganese concentration of surface waters may be elevated above naturally high levels when increased surface disturbance or erosion occurs. Elevated iron and manganese in the water can contribute to increased turbidity, reduced primary productivity, and avoidance by visual feeders such as

Arctic grayling. Concentrations greater than 2.0 mg/L iron may also cause significant invertebrate and fish egg losses, due to suffocation from precipitated iron hydroxide (Goettl and Davies 1977), suggesting that these potential downstream impacts should be further investigated.

Copper concentrations in water were slightly elevated at several sites in comparison to most unpolluted waters, which range from 0.001 - 0.005 mg/L (Moore and Ramamoorthy 1984). Sites with elevated copper included the Hogatza, Dulbi, and Gisasa rivers in 1986, the Hogatza and Koyukuk rivers in 1987, and the Hogatza, Koyukuk, and Bonanza drainages in 1988. Elevated copper concentrations are not uncommon in interior Alaska rivers and creeks (Snyder-Conn et al. 1992). The concentrations found are unlikely to impact adult fish, but could result in acute toxicity to sensitive juvenile Arctic grayling (Buhl and Hamilton 1990), as well as subchronic effects such as avoidance by salmonids (Giattina et al. 1982). Hyperactivity, reduced exploratory activity, and reduced migration are other behavioral changes induced in salmonids in the range of .005 - .060 mg/L copper (see review by Sorensen 1991). Since a large fraction of the copper present in the water was dissolved copper (see 1988 data set), concentrations in the range reported could induce such effects. Also, toxicity of mercury could be enhanced by the synergistic action of copper and mercury on aquatic organisms (Corner and Sparrow 1956 in Wershaw 1970). However, acclimation to high copper concentrations in water may mute these responses (Dixon and Sprague 1981).

Nickel concentrations in water at a number of refuge sites also appear to be slightly higher than those usually reported for unpolluted freshwater (0.001 - 0.003 mg/L, dissolved Ni) (Moore and Ramamoorthy 1984), but not sufficiently high to result in any likely adverse effects (EPA 1986).

The 1988 data set also disclosed significant differences among sites in total and dissolved iron concentrations, with the Hogatza River and Bonanza Creek containing more iron than other sites, especially Clear Creek, which had the lowest iron concentrations. Since all drainages have been influenced by mining, at least historically, it is not possible to discriminate between differences attributable to mining and natural among-site variability until additional unmined reference sites in each area are studied.

Sediment samples were only collected in 1987 and 1988. Statistical comparisons revealed significant differences among sites in the concentrations of a number of trace elements. In both 1987 and 1988, Site 2 (Koyukuk River) and 5 (Bonanza Creek) sediments contained significantly more copper and nickel than observed in Site 4 (Clear Creek) sediment, with the lowest concentration of these metals. The concentration of copper and nickel in sediments at Sites 2 and 5 were also enriched compared to most unpolluted freshwater sediment (Moore and Ramamoorthy 1984). Also, Site 2 was enriched in strontium compared to all other sites. In 1987, the only year when quality control criteria were met for arsenic, Sites 2 and 5 were also significantly enriched in this metalloid ( $\bar{x}$  = 12.3 and 13.0 mg/kg, respectively) compared to all other sites. The incomplete digestion procedure for arsenic and other elements in sediments may underestimate total arsenic, but, assuming this bias is slight, arsenic

concentrations appear to fall within the normal range (5 - 15 mg/kg) of uncontaminated freshwater sediment (Moore and Ramamoorthy 1984).

Sufficient northern pike were obtained for trace element analysis and statistical treatment from all study sites except Site 4, where only Arctic grayling were obtained. Generally, concentrations of trace elements in pike and grayling muscle appear normal in relation to fish elsewhere (Jenkins 1980, Wren et al. 1983), and among-site differences were not consistently demonstrated in metal content of fish muscle samples. No arsenic, beryllium, cadmium, or silver were found in any fish muscle sample, and boron, lead, and thallium were only detected in one muscle sample each from the two years of sampling. Other metals rarely detected in the fish muscle tissues include antimony, chromium, molybdenum, and nickel. However, Caribou Creek pike muscle concentrations of chromium are of interest. All five northern pike contained detectable chromium ( $\bar{x}$  = 0.86, range 0.49 - 1.40 mg/kg), concentrations that appear slightly elevated (Jenkins 1980, Moore and Ramamoorthy 1984). These concentrations are not anticipated to pose any problem to the fish, since chromium is rapidly depurated and the concentrations are not particularly high, but may indicate a source of chromium in the area.

Barium, copper, iron, magnesium, manganese, selenium, strontium, tin, and zinc were detected in most or all fish muscle samples. Three unusually high copper concentrations were observed in northern pike collected in 1988, including two fish from Bonanza Creek and one fish from Caribou Creek, but the significance of these levels in tissues is unknown. Similarly, one unusually high nickel concentration and two relatively high zinc concentrations were observed in fish tissue in the 1988 data set.

Similar results were observed when liver concentrations were examined. Antimony, arsenic, beryllium, lead, nickel, thallium, and vanadium were either rarely detected or not detected in refuge fish. One unusual finding was the occurrence of silver in one pike liver from Site 3 (Bishop Creek) in 1987 (at a concentration of 1.61 mg/kg). No published data for silver in fish tissues were located, so this finding is difficult to interpret. Silver was also noted in some northern pike muscle and liver samples from the Nowitna Refuge nearby, but these data were of questionable acceptability (USFWS, unpublished). Boron was also rarely detected in northern pike livers, but was observed in all three grayling analyzed from Site 4. Concentrations of boron in the grayling (1.2 - 2.9 mg/kg) indicate some exposure to boron, but not at concentrations high enough to induce toxicity (Thompson et al. 1976, Eisler 1990). Barium, cadmium, chromium, molybdenum, and vanadium were present in some fish livers, while copper, iron, magnesium, manganese, selenium, tin and zinc were present in all fish livers. The concentrations of these metals appear to fall within normal ranges for northern pike. Chromium concentrations in liver samples did not correspond with concentrations in muscle samples, confounding any interpretation of site differences in this metal. Significant among-site differences were found in the concentration of tin in pike livers, but these differences were not large.

Fish kidneys were only analyzed in 1987. Antimony, rarely detected in muscle or liver tissue, was detected in all the pike kidneys analyzed from Sites 2, 3, and 5. The highest cadmium concentration observed, 8.00 mg/kg in a northern pike from Site 5, is anomalously high. Silver was detected in the kidney (at a concentration of 3 mg/kg) from the same Site 3 pike with silver in its liver. Other metals were present in concentrations that appear within the normal range. Again, no among-site differences were noted except in the concentration of tin, which was highest at Site 3 (Bishop Creek) and Site 6 (Caribou Creek).

The relationship between fish metrics and site was also investigated. No significant differences in northern pike length, weight, or condition index occurred among sites. Also, correlations between individual northern pike lengths, weights, and condition indices and trace element concentrations, when observed, appeared weak.

One unfortunate casualty of our quality control/quality assurance screening was mercury in all three media -- water, sediments, and fish tissues. Water samples were not analyzed within the required 28 days (APHA et al. 1981); hence, most, if not all, mercury present in the samples was probably lost prior to analysis. For sediment and fish tissues, spike recoveries and/or standard reference material recoveries were too high in 1987 and too low in 1988, indicating poor quantitation abilities in both years. Nevertheless, it is important to point out that, according to analytical results, mercury was probably present in fish muscle tissue, as well as other tissues, possibly at concentrations > 1 mg/kg wet weight mercury. Concern therefore remains that certain watersheds on these refuges may contain mercury-contaminated fish that present a health hazard to fish, wildlife, and subsistence users, particularly if use of these resources is heavy and/or frequent. Mercury should therefore remain a target analyte for future studies, together with other analytes of interest we have identified.

## Recommendations

1. Additional study of water, sediment, fish, and fish stomach contents should be conducted to quantify aluminum, cadmium, copper, iron, lead, manganese, nickel, mercury, and zinc in these matrices in refuge watersheds, and to define the geographic extent and potential sources of high concentrations. Mercury pore water samples should also be collected.
2. Sampling should include reference drainages, as well as formerly mined and actively mined tributaries already examined. Study sites both above and below active and recently mined sites should be added, including sites near mines on Bear, Dry Camp, and Bishop creeks.
3. Discharge measurements should be made in conjunction with water and sediment sampling to evaluate possible causal relationships between discharge, turbidity and metal loading in the water column.
4. To improve statistical confidence in site differences, at least 10 adult northern pike should be obtained from each waterbody and data should be obtained on movement of northern pike within the study area. (Salmon at locations of local subsistence fisheries should also be sampled.) Resident species and summer breeders, particularly top predators such as mink or otter and raptors, should be sampled from selected waterbodies to obtain baseline data on biomagnification of metals such as mercury.
5. Skin, muscle, and liver tissues of fish should be analyzed, since partitioning among these tissues can provide information on point sources of mercury and other metals. Primary growth feathers from birds and hair from mammals will also provide information on local metal distribution.
6. Since snowmelt can result in episodic acidification which may act to release metals into the water column, water quality measurements should be made at sites following breakup to identify acidic streams and tributaries in the refuge. Sample collections should then focus on low pH, poorly buffered systems which are at greater risk.
7. Field blanks and spiked samples should be submitted to the analytical laboratory together with actual samples to better evaluate laboratory performance. Small single-matrix catalogs should be submitted to assure sufficient numbers of duplicates, spikes and standard reference of the same matrix as submitted samples.

8. Water samples collected at each site should be submitted separately for analysis of mercury within 28 days of collection. Teflon containers are recommended.
9. Detailed study plans should be developed in cooperation with the Alaska Departments of Fish and Game and Environmental Conservation.
10. Reanalysis should be required if stated holding times and quality assurance/quality control objectives for mercury are not met by the analytical laboratory.
11. Acid-volatile sulfides and total organic carbon should be measured in water and sediments to better estimate the bioavailability of metals present.
12. Other measures of fish health (e.g., gill histopathology, tumor rates, liver:body weight ratios) and ecosystem health (e.g., species diversity and abundance patterns; indicator species) should be incorporated into study plans.
13. The Alaska Departments of Environmental Conservation and Fish and Game and the Alaska Section of Epidemiology should review future data sets jointly with the Service to allow full agreement on its interpretation.

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## Appendix A

### Documentation and Sample Handling

#### *Study Proposals*

The 1986 sampling did not include a study plan. Study proposals were submitted for the 1987 and 1988 detailed studies. Study plans were prepared by Koyukuk NWR personnel, and subsequently reviewed and approved by the Fairbanks Environmental Contaminants Specialist and the Service's Region 7 (Alaska) Environmental Contaminants Coordinator following any needed revisions. The 1987 and 1988 study plans included objectives of the study, a discussion of the justification for the studies including a review of related research, a methods section including discussion of collection and analysis procedures, topographic maps indicating anticipated sample locations, and a cost proposal based on number and types of samples to be collected. In addition to selection of mined sites for sampling, one or more reference sites, believed to be unaffected by mining, were identified as controls for this study after review of the mining history of the area, including past and active placer and other mine sites on both State and Federal lands within and surrounding the refuge boundaries.

#### *Field Documentation*

During field studies, sample documentation was recorded in a weatherproof field notebook in permanent ink. The date and time of collections at each site was 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, tissue weights (if applicable), fork length, and 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, date of collection, type of sample or tissue, species (for fish), sample location, sample weight or volume, and analyses requested for each particular sample.

For the studies of Koyukuk and Innoko NWR's, 1986 - 1987 catalogs were submitted to the following analytical laboratories:

Catalog	Regional I.D.	Laboratory	Address	Analysis Date <sup>a</sup>
367	R78621NAES	Environmental Trace Substances Research Center	Route 3 Columbia, MO 65201	3/12/87
5433	R78729F	Hazelton Laboratories America	3301 Kinsman Blvd. P.O. Box 7545 Madison, WI 53707	10/24/87
5752	R788120	Versar, Inc.	6850 Versar Center Springfield, VA 22151	3/19/90

<sup>a</sup> These dates are approximations, based on information in the data sets and date of receipt of data. Analyses required several days. Where possible the date of the water analyses is presented.

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. Analytical data from catalogs for this project were received on 12 March 1987 (367), 27 October 1989 (5433), and 16 July 90 (5752).

#### *Chain of Custody*

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

#### *Sample Preservation/Storage*

Following collection, unfiltered water samples were immediately preserved with Ultrix nitric acid to a pH < 2. Unfiltered water samples in 500-ml containers were preserved with 1.5 ml acid and filtered samples were preserved with 0.75 ml nitric acid. Water, sediment, and fish samples were placed in coolers with ice, commercial ice packs, or snow, and transported by

boat or float plane to Galena, Alaska for temporary storage. Water samples were refrigerated from the date of collection until shipment; sediment and fish tissues were kept frozen.

#### *Sample Shipment*

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

#### *Sample Holding Times*

Holding times for Catalogs 367, 5433, and 5752 were 5 months, 5 months, and 9 months, respectively. The prescribed holding time for mercury in water is 28 days; the maximum recommended holding time for other metals in water is 6 months (APHA et al. 1989). No holding times have been established for metals in sediments or tissues; however, it is widely assumed that loss from these media by volatilization or plating onto the container wall would be minimal. Based on the prolonged holding times, mercury is likely to have been lost from the water samples and those results should be considered invalid. For other metals, particularly cadmium, significant losses may have also occurred in water samples in 1988. However, the analysis date in relation to the holding time probably resulted in only small losses. Refrigeration, in addition to acidification, may have mitigated loss of these metals. It is uncertain whether losses due to excessive holding time in 1988 are truly important.

## Appendix B

### Sample Identification and Data Base Management

#### *General*

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

#### *Contaminants Database Entry Fields*

##### Sample Identification Fields

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

T	Type/tissue	L	Liver	See codes
Auxiliary Fields				
SEX		M, F, U	Male, female or unknown	Samples of biota only
DATE	Sample date	12/13/90		
SPECIES	Genus and species	Homo sapiens	Human	Samples of biota only
NO IN COMP	Number of Organisms in composite sample	18	If 18 sculpin were in a sample	Samples of biota only
SAMPLE WT	Weight of submitted sample in grams	43	43 gm = weight of liver	Weight of discrete organs or subsamples
TOTAL WT	Total weight of organism or sample if subsampled	100	100 gm = weight of whole fish	Weight of whole, original sample or organism
TLGTH	Organism's total length (mm)	25	25 mm = total length of fish	Samples of biota only
FLGTH	Fork length (mm)	23	23 mm = fork length of fish	Fish only
UNIT	Unit of analysis	ppm, ppb	(mg/L, mg/kg, µg/L, µg/kg)	Other units possible
MOIST	% moisture	45	45% moisture	All matrices except water
BASIS	Basis for data reported	wet or dry	Wet or dry weight	All matrices except water <sup>3</sup>
Detection Limit (shown as X and the metal symbol)	Less than for each metal	<	Used when value measured is less than detection limit	
As (Example)	Metal concentration	5.5	5.5 mg/kg	See basis and unit

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

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

<sup>3</sup> Concentrations in water are always reported on a wet weight basis. However, labs vary in how other matrices are reported.

### General Location Codes

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

### Species Codes

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

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

If the study involves known species, use these codes:

#### Fish

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

#### Birds

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

#### Type/Tissue Codes

N - brain	P - bone	B - bile
O - blood	C - carcass	L - liver
K - kidney	M - muscle	W - whole (tissue or sediment)
G - gill	E - egg	H - hair
F - feather	D - dissolved metals (H <sub>2</sub> O)	T - total metals (H <sub>2</sub> O)
R - tot. recoverable metals (H <sub>2</sub> O)	V - leaves	Z - stem
U - shoots	S - stomach	A - sand (2.0 to .0625mm)
L - clay (<.0039mm)	I - silt (.0625 to .0039mm)	

## Appendix C

### Quality Assurance/Quality Control (QA/QC) of Chemical Analyses

#### *General*

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 (PACF), Patuxent National Wildlife Research Center (PACF), Laurel, Maryland, to determine the inorganic and organic composition of samples.

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

1. A brief description of the methods used in the analysis.
2. The analytical results.
3. Results of any QA/QC samples analyzed in conjunction with the reported catalog, including:
  - a. Limits of detection for each sample
  - b. Duplicate analysis
  - c. Spiked sample analysis
  - d. Standard reference material (SRM) analysis
  - e. Procedural blank analysis
4. A description of any problems encountered in the analysis.

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

QA/QC samples were subjected to a rigorous software program, dubbed Saint Patrick (an allusion to Saint Peter's decision-making power), written in Dbase IV<sup>®</sup>. This screening program was designed by Patrick Scannell, Ecological Services, Fairbanks. Parameters and screening criteria utilized in this software are presented below.

### *Limits of Detection*

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

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

In determining the LOD, the moisture adjustment is more significant if the sample is analyzed as a wet sample than if the sample is freeze-dried first, or is naturally dry (e.g., hair samples). The smaller the sample size, after moisture adjustment, the higher will be the limit of detection limit for that 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. For general reference, however, the general method limits for this catalog are reported in the methods section of the report.

### *Analytical Precision*

Precision refers to the degree of agreement among repeated measurements of a given sample at the same time, and is not a measure of accuracy (the correctness of the measurement). Precision varies with such factors as the homogeneity of the sample, sample volume, sample matrix, instrumental method, instrumental drift, chemical interferences, and the analyte concentration in the sample.

Estimates of precision for this study were made using duplicate analysis, where two separate subsamples of a homogenized sample are collected and analyzed by the contract laboratory. While this method of creating duplicates lacks the measurement errors associated with improper or incomplete mixing of samples split in the field, it may entail bias by the laboratory, since the expected result is known. Precision is monitored by the contract laboratory by using range ratio control charts for each analyte (metal) and matrix (water, sediment, tissue). For our screening of data, the measure selected for estimating precision is the relative percent difference (RPD):

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

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

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

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

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

Table C-1. *Acceptable average precision measured as relative percent difference (RPD) for each analyte based on the limit of detection (LOD)*

Method	Average Required RPD <10x LOD	Average Required RPD >10x LOD
ICP SCAN <sup>a</sup>	200%	33.3%
ATOMIC ABSORPTION	200%	33.3%

<sup>a</sup> Inductively coupled plasma emission spectroscopy, including direct and preconcentrated scans.

The criteria selected for precision (above) are not particularly rigorous. However, since replicate sampling occurred at all sites, these criteria probably ensure adequate average precision for the prescribed use of the data.

### *Analytical Accuracy*

#### Spiked Samples

In addition to precision, measurements of correctness of the analytical analysis are needed to guarantee the quality of the data that are semiquantitative (>2 LOD) or quantitative (>10 LOD) and to estimate chemical interferences that may occur with particular types of samples. One method used by USFWS contract laboratories to estimate accuracy and gauge interference is that of spiked samples. After a sample in the sample catalog is homogenized, two separate subsamples are taken. One is analyzed as a sample. The other subsample is "spiked" with a known quantity of one or more analytes, and then analyzed. The difference between the two subsamples, after accounting for any differences in sample weight, is the spike recovery. This value is usually reported as a percentage of the amount added. Recovery rates greater than 100% may indicate that the instrument was incorrectly calibrated, subject to upward drift since the original calibration, or that contamination of the sample may have occurred. If the spike recovery is less than 100%, then the analyte was not fully recovered. This could occur due to loss of the analyte during the sample procedure (e.g., loss of mercury due to volatility), instrument drift following initial calibration, errors in the calibration procedure, or chemical interferences inherent in the particular matrix being analyzed. Another important source of incomplete metal recoveries is incomplete digestion of the sample material. Unless otherwise specified, metal digestions of sediments performed by contract laboratories are incomplete, resulting in the release of some, but not all, of the analyte. 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, either by chemical complexing or by physical processes, may not become biologically

available under any natural circumstance. In contrast, the digestions of both water and tissue samples were complete, in order to release all metals in these matrices.

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

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

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

Table C-2. Acceptable Accuracy for recovery of spiked samples by method, based on Fish and Wildlife Service criteria presented by Moore (1990) and APHA et al. (1989)

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

<sup>a</sup> ICP = inductively coupled plasma emission spectroscopy, including direct and preconcentrated scans.

<sup>b</sup> Including cold vapor, hydride generation, and graphite furnace AA.

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

## Standard Reference Materials

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

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

Certified values provided by the source are usually determined by repeated analysis of the analyte using several different methods (e.g., atomic absorption spectrometry, X-ray fluorescence, and inductively coupled plasma spectrometry). The certified value for each analyte, or "true value," is typically the weighted mean of the different methods. A standard deviation is also calculated and used to provide a certified range. The method for creating this range varies somewhat depending on source of the analyte, but is supposed to provide a 95% confidence interval about which values different from the certified value might actually occur due to variability in the SRM as well as the methodology. In some cases, a considerable amount of professional judgement is used to define this range.

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

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

If the mean value of an analyte as measured by the laboratory is inside the range of the certified value  $\pm 3$  SD, the SRM data are considered acceptable or "good". For certified values  $\geq 2$  LOD, a printout is also given of analytes for which the measured values fall outside  $\pm 3$  SD; these data are listed as questionable. On the QA/QC Summary Sheet for each catalog (Appendix D), "Low SRM" and "High SRM" show this confidence interval.

Where the SD is not known, it is defined as 10% of the certified value, and the same range is allowed as above. Use of 10% as the estimated standard deviation is based on examination of the average relationship between the mean and standard deviation for several NIST SRM's for a suite of metals. Typically, the standard deviation is 5 - 10% of the true value.

In this test, if no certified value for the analyte is available, the consensus value  $\pm 3$  standard deviations is used to screen performance.

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

The more SRM's used on a given matrix, the higher the probability that the laboratory will fail to meet acceptance criteria defined above in all tests. The final screening criterion developed for SRM evaluation avoids penalizing laboratories for performing additional testing. When more than one comparison with a given SRM is performed, the mean measured value is compared to the true value (or consensus value)  $\pm 3$  SD. Occasionally this average measured SRM value is less than twice the LOD. In this case, "AvgSRM < 2 \* LOD" appears on the QA/QC Summary Sheet. If two different SRM's are used for the same matrix and analytes, then each measured value is compared to the acceptable range for that SRM, and the Z-Score is averaged. In the QA/QC Summary Sheet, the Z-score (also known as a standard score) is given for each analyte by SRM. This score indicates how many SD's above or below the mean the measured value of the SRM falls. All Z scores outside the range of the certified value  $\pm 3$  SD are also sorted to the "Questionable Quality Data" report.

### *Blanks*

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

In the case of the Koyukuk samples, no field blanks were collected. However, field blanks were collected using the same sample containers and same acid preservation at the Arctic National Wildlife Refuge in 1988. No contaminants were detected during subsequent metals



analysis, indicating that the sample containers and acid were probably contaminant-free. However, incidental contamination of water samples from dust or filtration equipment (dissolved metals samples) cannot be ruled out.

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

The laboratory may run a single blank through the entire analytical process, including sample preparation and reagent treatment. If contaminants detected during the entire process are negligible, then separate sample preparation and reagent blanks are not necessary. Also, if blank contaminant levels are recurring (i.e., nonrandom), the data set may be developed by blank subtraction. If contaminants are detected at levels that may compromise the results of the analysis and are not systematic, the above breakdown is needed to identify sources of contamination. Blank samples used in quality control for sample catalogs are summarized in Appendix D.

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

**Appendix D**

**Quality Assurance/Quality Control Screening Results  
(Raw Data)**

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QAQC SUMMARY FOR : 86 KOYUKUK 367/METALS/10 WATER  
FOR MATRIX: WaterT and METHOD: AA

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Antimony	1	0.00	1	110.0	1	0.0004	0.0004
Arsenic	1	20.41	1	100.0	1	0.0005	0.0005
Mercury	1	0.00	1	100.0	1	0.0004	0.0004

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QAQC SUMMARY FOR : 86 KOYUKUK 367/METALS/10 WATER  
FOR MATRIX: WaterT and METHOD: ICP

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Cadmium	1	0.00	1	100.0	1	0.0003	0.0003
Copper	1	1.71	1	103.0	1	0.0008	0.0008
Iron	1	1.10	1	99.0	1	0.2390	0.2390
Lead	1	0.00	1	101.0	1	0.0070	0.0070
Molybdenum	1	0.00	1	99.0	1	0.0006	0.0006
Nickel	1	11.18	1	102.0	1	0.0020	0.0020
Selenium	1	0.00	1	110.0	1	0.0060	0.0060
Thallium	1	0.00	1	100.0	1	0.0100	0.0100
Vanadium	1	0.00	1	101.0	1	0.0002	0.0002
Zinc	1	0.00	1	97.0	1	0.0014	0.0014

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QAQC SUMMARY FOR : 86 KOYUKUK 367/METALS/10 WATER  
FOR MATRIX: WaterT and METHOD: AA

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Antimony	0.0720	0.0728	0.1092	ERA9601TM	0.0004	-2.0900
Arsenic	0.0390	0.0352	0.0528	ERA9601TM	0.0005	-1.1400
Mercury	0.0051	0.0036	0.0052	ERA9601TM	0.0004	1.7500

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10/13/92QAQC SUMMARY FOR : 86 KOYUKUK 367/METALS/10 WATER  
FOR MATRIX: WaterT and METHOD: ICPF

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Cadmium	0.1250	0.1120	0.1680	ERA 9401	0.0003	-1.0700
Copper	0.1710	0.1320	0.1980	ERA 9401	0.0008	0.3600
Iron	0.5810	0.4560	0.6840	ERA 9401	0.2390	0.1900
Lead	0.4200	0.3120	0.4680	ERA 9401	0.0070	0.7700
Molybdenum	0.1650	0.1320	0.1980	ERA 9401	0.0006	0.0000
Nickel	0.2200	0.1720	0.2580	ERA 9401	0.0020	0.2300
Selenium	0.0520	0.0456	0.0684	ERA 9401	0.0060	-0.8800
Thallium	0.0700	0.0488	0.0732	ERA 9401	0.0100	1.4800
Vanadium	0.0400	0.0336	0.0504	ERA 9401	0.0002	-0.4800
Zinc	0.2860	0.2320	0.3480	ERA 9401	0.0014	-0.1400

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QAQC SUMMARY FOR : 87 KOYUKUK/CATALOG/5433/METALS  
FOR MATRIX: Animal and METHOD:

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
	0	0.00	0	***.*	0	-9.0000	0.0000

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QAQC SUMMARY FOR : 87 KOYUKUK/CATALOG/5433/METALS  
FOR MATRIX: Animal and METHOD: AA

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Antimony	5	7.41	5	86.5	4	-9.0000	0.0000
Mercury	5	5.74	5	98.0	4	-9.0000	0.0000
Thallium	5	0.00	5	95.2	4	-9.0000	0.0000

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QAQC SUMMARY FOR : 87 KOYUKUK/CATALOG/5433/METALS  
FOR MATRIX: Animal and METHOD: ICP

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Aluminum	6	18.20	5	98.8	4	-9.0000	0.0000
Barium	6	0.00	5	104.2	4	-9.0000	0.0000
Beryllium	6	0.00	5	100.4	4	-9.0000	0.0000
Boron	6	62.39	5	109.2	4	-9.0000	0.0000
Cadmium	6	0.00	5	94.6	4	-9.0000	0.0000
Chromium	6	14.81	5	106.4	4	-9.0000	0.0000
Copper	6	64.57	5	97.0	4	-9.0000	0.0000
Iron	6	70.62	5	79.4	4	-9.0000	0.0000
Lead	6	0.00	5	91.0	4	-9.0000	0.0000
Magnesium	6	33.72	5	97.0	4	-9.0000	0.0000
Manganese	6	29.91	5	103.2	4	-9.0000	0.0000
Molybdenum	6	42.11	5	99.2	4	-9.0000	0.0000
Nickel	6	15.24	5	100.8	4	-9.0000	0.0000
Silver	6	0.00	5	101.8	4	-9.0000	0.0000
Strontium	6	57.76	5	112.0	3	-9.0000	0.0000
Tin	6	20.43	5	90.4	2	-9.0000	0.0000
Vanadium	6	0.00	5	100.6	4	-9.0000	0.0000
Zinc	6	46.84	5	80.2	4	-9.0000	0.0000

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QAQC SUMMARY FOR : 87 KOYUKUK/CATALOG/5433/METALS  
FOR MATRIX: Sediment and METHOD: AA

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Antimony	1	1.73	1	91.0	1	-9.0000	0.0000
Arsenic	1	12.11	1	93.0	1	-9.0000	0.0000
Mercury	1	0.00	1	116.0	1	-9.0000	0.0000
Thallium	1	0.00	1	85.4	1	-9.0000	0.0000

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Aluminum	1	0.88	1	91.0	1	-9.0000	0.0000
Barium	1	0.60	1	103.0	1	-9.0000	0.0000
Beryllium	1	0.00	1	96.0	1	-9.0000	0.0000
Boron	1	0.00	1	87.0	1	-9.0000	0.0000
Cadmium	1	0.00	1	102.0	1	-9.0000	0.0000
Chromium	1	0.83	1	99.0	1	-9.0000	0.0000
Copper	1	2.16	1	100.0	1	-9.0000	0.0000
Iron	1	0.00	1	96.0	1	-9.0000	0.0000
Lead	1	0.00	1	119.0	1	-9.0000	0.0000
Magnesium	1	0.22	1	95.8	1	-9.0000	0.0000
Manganese	1	0.31	1	105.0	1	-9.0000	0.0000
Molybdenum	1	0.00	1	114.0	1	-9.0000	0.0000
Nickel	1	1.20	1	98.5	1	-9.0000	0.0000
Silver	1	0.00	1	93.0	1	-9.0000	0.0000
Strontium	1	2.47	1	97.0	1	-9.0000	0.0000
Tin	1	0.00	1	100.0	1	-9.0000	0.0000
Vanadium	1	0.61	1	94.2	1	-9.0000	0.0000
Zinc	1	2.28	1	103.0	1	-9.0000	0.0000

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Antimony	1	0.00	1	95.0	2	-9.0000	0.0000
Arsenic	1	0.00	1	85.0	1	-9.0000	0.0000
Mercury	1	0.00	1	102.0	2	-9.0000	0.0000
Thallium	1	0.00	1	95.8	2	-9.0000	0.0000

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Aluminum	1	6.90	1	76.0	2	-9.0000	0.0000
Barium	1	0.00	1	97.5	2	-9.0000	0.0000
Beryllium	1	0.00	1	90.0	2	-9.0000	0.0000
Boron	1	0.00	1	70.0	2	-9.0000	0.0000
Cadmium	1	0.00	1	92.6	2	-9.0000	0.0000
Chromium	1	66.67	1	84.2	2	-9.0000	0.0000
Copper	1	0.00	1	93.3	2	-9.0000	0.0000
Iron	1	3.71	1	78.0	2	-9.0000	0.0000
Lead	1	21.94	1	108.0	2	-9.0000	0.0000
Magnesium	1	0.00	1	88.4	2	-9.0000	0.0000
Manganese	1	0.00	1	92.5	2	-9.0000	0.0000
Molybdenum	1	0.00	1	89.0	2	-9.0000	0.0000
Nickel	1	0.00	1	92.5	2	-9.0000	0.0000
Silver	1	0.00	1	98.2	2	-9.0000	0.0000
Strontium	1	15.38	1	92.0	2	-9.0000	0.0000
Tin	1	0.00	1	84.8	2	-9.0000	0.0000
Vanadium	1	0.00	1	92.4	2	-9.0000	0.0000
Zinc	1	9.52	1	89.5	2	-9.0000	0.0000

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QAQC SUMMARY FOR : 87 KOYUKUK/CATALOG/5433/METALS  
FOR MATRIX: Animal and METHOD: AA

10:02:43

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Antimony	2.9625	2.3000	3.5000	NBS 1571	0.0000	0.2100
Mercury	1.7500	1.3300	1.6100	NBS 2704	0.0000	4.0000
Thallium	4.9925	4.0000	6.0000	SPEX WP-11	0.0000	-0.0200

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QAQC SUMMARY FOR : 87 KOYUKUK/CATALOG/5433/METALS  
FOR MATRIX: Animal and METHOD: ICP

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Aluminum	<5.0000	1.6000	2.4000	NBS 1577A	0.0000	
Cadmium	0.2625	0.3200	0.5600	NBS 1577A	0.0000	-2.9600
Copper	138.2500	144.0000	172.0000	NBS 1577A	0.0000	-2.8200
Iron	159.2500	154.0000	234.0000	NBS 1577A	0.0000	-1.7400
Lead	<5.0000	0.1050	0.1650	NBS 1577A	0.0000	
Magnesium	506.2500	570.0000	630.0000	NBS 1577A	0.0000	-6.2500
Manganese	9.3000	8.3000	11.5000	NBS 1577A	0.0000	-0.7500
Molybdenum	2.7500	2.5000	4.5000	NBS 1577A	0.0000	-1.5000
Silver	<2.5000	0.0200	0.0600	NBS 1577A	0.0000	
Strontium	<0.4875	0.1320	0.1440	NBS 1577A	0.0000	
Zinc	117.7500	107.0000	139.0000	NBS 1577A	0.0000	-0.6600

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QAQC SUMMARY FOR : 87 KOYUKUK/CATALOG/5433/METALS  
FOR MATRIX: Sediment and METHOD: AA

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Antimony	3.1600	2.3000	3.5000	NBS 1571	0.0000	0.8700
Arsenic	0.3550	0.3280	0.4920	RICE FL 1568	0.0000	-1.3400
Mercury	1.6100	1.3300	1.6100	NBS 2704	0.0000	2.0000
Thallium	1.5200	0.9200	1.2000	NBS 2704	0.0000	6.5700

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QAQC SUMMARY FOR : 87 KOYUKUK/CATALOG/5433/METALS  
FOR MATRIX: Sediment and METHOD: ICP

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score	Comments
		Low SRM	Hi SRM				
Aluminum	12800.0000	57900.0010	64300.0010	NBS 2704	0.0000	-30.1900	
Barium	89.6000	390.0000	438.0000	NBS 2704	0.0000	-27.0300	
Cadmium	4.5000	3.0100	3.8900	NBS 2704	0.0000	4.7700	
Chromium	75.6000	125.0000	145.0000	NBS 2704	0.0000	-11.8800	
Copper	88.6000	88.6000	108.6000	NBS 2704	0.0000	-2.0000	
Iron	30000.0000	39100.0000	43100.0000	NBS 2704	0.0000	-11.1000	
Lead	165.0000	127.0000	195.0000	NBS 2704	0.0000	0.2400	
Magnesium	8380.0000	11600.0000	12400.0000	NBS 2704	0.0000	-18.1000	
Manganese	470.0000	517.0000	593.0000	NBS 2704	0.0000	-4.4700	
Nickel	35.9000	38.1000	50.1000	NBS 2704	0.0000	-2.7300	
Vanadium	22.8000	87.0000	103.0000	NBS 2704	0.0000	-18.0500	
Zinc	383.0000	414.0000	462.0000	NBS 2704	0.0000	-4.5800	

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QAQC SUMMARY FOR : 87 KOYUKUK/CATALOG/5433/METALS  
FOR MATRIX: Wacart and METHOD: AA

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Antimony	5.2000	2.3000	3.5000	SPEX WP-11	0.0000	7.5700
Arsenic	9.4000	8.0000	12.0000	SPEX EP-8	0.0000	-0.6000
Mercury	10.0000	8.0000	12.0000	SPEX EP-8	0.0000	0.0000
Thallium	5.2000	4.0000	6.0000	SPEX WP-11	0.0000	0.4000

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Aluminum	0.1820	0.1060	0.2460	ERA9911TM	0.0000	0.1700
Barium	0.1080	0.0640	0.1520	ERA9911TM	0.0000	0.0000
Beryllium	0.0610	0.0400	0.0960	ERA9911TM	0.0000	-0.5000
Boron	0.3600	0.1740	0.4060	ERA9911TM	0.0000	1.2100
Cadmium	0.0890	0.0560	0.1320	ERA9911TM	0.0000	-0.2600
Chromium	0.1610	0.1110	0.2590	ERA9911TM	0.0000	-0.6500
Copper	0.1410	0.0830	0.1950	ERA9911TM	0.0000	0.0700
Iron	0.2260	0.1390	0.3230	ERA9911TM	0.0000	-0.1100
Lead	0.1560	0.0830	0.1950	ERA9911TM	0.0000	0.6100
Magnesium	<0.2500	20.0000	32.0000	ERA9911TM	0.0000	
Manganese	0.1290	0.0780	0.1820	ERA9911TM	0.0000	-0.0400
Molybdenum	0.1840	0.1220	0.2820	ERA9911TM	0.0000	-0.4500
Nickel	0.3570	0.2050	0.4810	ERA9911TM	0.0000	0.2000
Silver	0.0420	0.0260	0.0620	ERA9911TM	0.0000	-0.2200
Vanadium	0.1710	0.1070	0.2510	ERA9911TM	0.0000	-0.2200
Zinc	0.1820	0.1050	0.2450	ERA9911TM	0.0000	0.2000

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QAQC SUMMARY FOR : 88 KOY/CAT 5752/WAT, SED, FISH/MT  
FOR MATRIX: Animal and METHOD:

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
	0	0.00	0	***.*	0	-9.0000	0.0000

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QAQC SUMMARY FOR : 88 KOY/CAT 5752/WAT, SED, FISH/MT  
FOR MATRIX: Animal and METHOD: AA

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Arsenic	3	0.00	3	101.8	3	-9.0000	0.5000
Mercury	3	6.06	3	59.8	3	-9.0000	0.1000
Selenium	3	10.12	3	114.7	3	-9.0000	0.5000

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QAQC SUMMARY FOR : 88 KOY/CAT 5752/WAT, SED, FISH/MT  
FOR MATRIX: Animal and METHOD: ICP

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Aluminum	4	59.02	4	98.6	3	-9.0000	3.5000
Antimony	4	0.00	4	26.6	4	-9.0000	5.0000
Barium	4	37.18	4	97.5	4	0.1540	0.5000
Beryllium	4	0.00	4	105.0	4	-9.0000	0.2000
Boron	4	15.79	4	92.0	4	1.1310	2.0000
Cadmium	4	1.94	4	97.9	4	-9.0000	0.5000
Chromium	4	38.80	4	99.3	4	0.7610	2.0000
Copper	4	5.82	4	97.9	4	0.3120	1.0000
Iron	4	10.56	4	90.7	4	2.0760	2.0000
Lead	4	32.63	4	95.8	4	-9.0000	4.0000
Magnesium	4	1.82	1	87.6	4	0.7690	2.0000
Manganese	4	27.79	4	103.2	4	0.2470	1.0000
Molybdenum	4	30.77	4	85.7	4	-9.0000	1.0000
Nickel	4	67.51	4	106.1	4	-9.0000	2.0000
Silver	4	0.00	4	1.9	4	-9.0000	1.0000
Strontium	4	61.63	4	98.7	4	-9.0000	2.0000
Thallium	4	0.00	4	102.0	4	-9.0000	10.0000
Tin	4	19.08	4	31.1	4	-9.0000	5.0000
Vanadium	4	20.90	4	94.2	4	-9.0000	1.0000
Zinc	4	4.99	4	96.0	4	1.7890	1.0000

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QAQC SUMMARY FOR : 88 KOY/CAT 5752/WAT, SED, FISH/MT  
FOR MATRIX: Sediment and METHOD: AA

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Arsenic	1	40.80	1	97.6	3	-9.0000	1.0000
Mercury	1	0.00	1	82.0	3	-9.0000	0.1000
Selenium	1	0.00	1	84.9	3	-9.0000	1.0000

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Aluminum	1	1.66	1	182.0	3	-9.0000	50.0000
Antimony	1	0.00	1	36.4	4	-9.0000	5.0000
Barium	1	1.29	1	88.0	4	0.1540	0.5000
Beryllium	1	2.74	1	94.8	4	-9.0000	0.1000
Boron	1	4.22	1	73.0	4	1.1310	1.0000
Cadmium	1	5.83	1	85.6	4	-9.0000	0.5000
Chromium	1	0.62	1	86.5	4	0.7610	1.0000
Copper	1	1.76	1	88.3	4	0.3120	0.5000
Iron	1	0.01	1	144.2	4	2.0760	10.0000
Lead	1	1.65	1	82.5	4	-9.0000	5.0000
Magnesium	1	0.82	1	108.6	4	0.7690	20.0000
Manganese	1	0.86	1	93.3	4	0.2470	0.5000
Molybdenum	1	24.05	1	81.4	4	-9.0000	1.0000
Nickel	1	2.57	1	90.6	4	-9.0000	2.0000
Silver	1	0.00	1	77.6	4	-9.0000	1.0000
Strontium	1	0.21	1	90.5	4	-9.0000	1.0000
Thallium	1	0.00	1	96.5	4	-9.0000	10.0000
Tin	1	28.34	1	80.8	4	-9.0000	10.0000
Vanadium	1	0.19	1	87.8	4	-9.0000	1.0000
Zinc	1	1.08	1	86.4	4	1.7890	1.0000

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Arsenic	2	0.00	2	90.7	2	-9.0000	0.0030
Mercury	1	0.00	1	99.0	2	-9.0000	0.0002
Selenium	2	0.00	2	103.0	2	-9.0000	0.0025

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Aluminum	2	10.76	2	113.1	2	8.3000	0.0500
Beryllium	2	0.00	2	62.2	2	-9.0000	0.0005
Cadmium	2	100.00	2	92.9	2	-9.0000	0.0010
Chromium	2	24.54	2	94.0	2	4.3000	0.0150
Copper	2	5.48	2	80.7	2	7.5000	0.0150
Iron	2	3.70	2	116.0	2	**.*	0.1500
Lead	2	38.60	2	98.0	2	10.9000	0.0150
Manganese	2	2.99	2	131.3	2	6.7000	0.0100
Nickel	2	29.08	2	92.5	2	-9.0000	0.0100
Thallium	2	0.00	2	99.0	2	-9.0000	0.0500
Tin	2	82.35	2	84.3	2	-9.0000	0.0300
Zinc	2	65.94	2	62.5	2	5.5000	0.0300

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QAQC SUMMARY FOR : 88 KOY/CAT 5752/WAT, SED, FISH/MT  
FOR MATRIX: WaterT and METHOD: AA

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Arsenic	2	0.00	2	90.7	2	-9.0000	0.0030
Mercury	1	0.00	1	99.0	2	-9.0000	0.0002
Selenium	2	0.00	2	103.0	2	-9.0000	0.0025

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QAQC SUMMARY FOR : 88 KOY/CAT 5752/WAT, SED, FISH/MT  
FOR MATRIX: WaterT and METHOD: ICP

ANALYTE	N	MEAN RPD	N	Mean Spike	N	MAX. BLANK	LOD
Aluminum	2	10.76	2	113.1	2	8.3000	0.0500
Beryllium	2	0.00	2	62.2	2	-9.0000	0.0005
Cadmium	2	100.00	2	92.9	2	-9.0000	0.0010
Chromium	2	24.54	2	94.0	2	4.3000	0.0150
Copper	2	5.48	2	80.7	2	7.5000	0.0150
Iron	2	3.70	2	116.0	2	**.*	0.1500
Lead	2	38.60	2	98.0	2	10.9000	0.0150
Manganese	2	2.99	2	131.3	2	6.7000	0.0100
Nickel	2	29.08	2	92.5	2	-9.0000	0.0100
Thallium	2	0.00	2	99.0	2	-9.0000	0.0500
Tin	2	82.35	2	84.3	2	-9.0000	0.0300
Zinc	2	65.94	2	62.5	2	5.5000	0.0300

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score	Comments
		Low SRM	Hi SRM				
Arsenic	1.9467	0.8500	4.0100	EPAFISH	0.5000	-0.6100	
Mercury	0.6400	0.6400	0.9600	NRC_CANADA	0.1000	-2.0000	
Selenium	2.1333	0.2960	0.4440	EPAFISHMETAL	0.5000	0.0000	Ref. Val. < LOD

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QAQC SUMMARY FOR : 88 KOY/CAT 5752/WAT, SED, FISH/MT  
FOR MATRIX: Animal and METHOD: ICP

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score	Comments
		Low SRM	Hi SRM				
Cadmium	0.5000	0.4000	0.6000	NRC_CANADA	0.5000	0.0000	AvgSRM < 2 * LOD
Chromium	2.8250	2.8800	4.3200	NRC_CANADA	2.0000	0.0000	AvgSRM < 2 * LOD
Copper	4.4500	4.1600	6.2400	NRC_CANADA	1.0000	-1.4400	
Iron	56.9250	50.8800	76.3200	NRC_CANADA	2.0000	-1.0500	
Lead	3.1000	0.3200	0.4800	NRC_CANADA	4.0000	0.0000	Ref. Val. < LOD
Magnesium	1101.8200	968.0000	1452.0000	NRC_CANADA	2.0000	-0.8900	
Manganese	1.0750	1.0400	1.5600	NRC_CANADA	1.0000	0.0000	AvgSRM < 2 * LOD
Nickel	1.2500	0.9600	1.4400	NRC_CANADA	2.0000	0.0000	Ref. Val. < LOD
Zinc	16.7750	17.0400	25.5600	NRC_CANADA	1.0000	-2.1200	

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10/13/92QAQC SUMMARY FOR : 88 KOY/CAT 5752/WAT, SED, FISH/MT  
FOR MATRIX: Sediment and METHOD: AA

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score	Comments
		Low SRM	Hi SRM				
Arsenic	1.9467	0.8500	4.0100	EPAFISH	1.0000	0.0000	AvgSRM < 2 * LOD
Mercury	0.6400	0.6400	0.9600	NRC_CANADA	0.1000	-2.0000	
Selenium	2.1333	0.2960	0.4440	EPAFISHMETAL	1.0000	0.0000	Ref. Val. < LOD

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QAQC SUMMARY FOR : 88 KOY/CAT 5752/WAT, SED, FISH/MT  
FOR MATRIX: Sediment and METHOD: ICP

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score	Comments
		Low SRM	Hi SRM				
Cadmium	0.5000	0.4000	0.6000	NRC_CANADA	0.5000	0.0000	AvgSRM < 2 * LOD
Chromium	2.8250	2.8800	4.3200	NRC_CANADA	1.0000	-2.1500	
Copper	4.4500	4.1600	6.2400	NRC_CANADA	0.5000	-1.4400	
Iron	56.9250	50.8800	76.3200	NRC_CANADA	10.0000	-1.0500	
Lead	3.1000	0.3200	0.4800	NRC_CANADA	5.0000	0.0000	Ref. Val. < LOD
Magnesium	1101.8200	968.0000	1452.0000	NRC_CANADA	20.0000	-0.8900	
Manganese	1.0750	1.0400	1.5600	NRC_CANADA	0.5000	-1.7300	
Nickel	1.2500	0.9600	1.4400	NRC_CANADA	2.0000	0.0000	Ref. Val. < LOD
Zinc	16.7750	17.0400	25.5600	NRC_CANADA	1.0000	-2.1200	

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score	Comments
		Low SRM	Hi SRM				
Arsenic	41.8100	0.0400	0.0600	NBSKY	0.0030	8352.0000	
Mercury	5.1500			EPA-LVKY	0.0002	0.0000	No Ref. Val.
Selenium	49.5500	0.0400	0.0600	NBSKY	0.0025	9900.0000	

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03/30/92QAQC SUMMARY FOR : 88 KOY/CAT 5752/WAT,SED,FIS/MT  
FOR MATRIX: WaterD and METHOD: ICP

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score	Comments
		Low SRM	Hi SRM				
Aluminum	2.1484	1.6000	2.4000	EPA LV	0.0500	0.7400	
Aluminum	20.0869	16.0000	24.0000	NBSKOY	0.0500	0.0400	
Aluminum	0.3268	0.4000	0.6000	NBSKY	0.0500	-3.4600	
Antimony	1.5609	3.2000	4.8000	NBSKOY	0.0030	-6.1000	
Barium	2.0075	1.6000	2.4000	NBSKOY	0.0000	0.0400	
Beryllium	0.5195	0.4008	0.6012	EPA LV	0.0005	0.3700	
Beryllium	2.0957	1.6000	2.4000	NBSKOY	0.0005	0.4800	
Beryllium	0.0131	0.0200	0.0300	NBSKY	0.0005	-4.7600	
Boron	1.9113	1.6000	2.4000	NBSKOY	0.0000	-0.4400	
Cadmium	0.4999	0.3936	0.5904	EPA LV	0.0010	0.1600	
Cadmium	2.0136	1.6000	2.4000	NBSKOY	0.0010	0.0700	
Cadmium	0.0198	0.0200	0.0300	NBSKY	0.0010	-2.0800	
Chromium	0.5074	0.4024	0.6036	EPA LV	0.0150	0.0900	
Chromium	2.0160	1.6000	2.4000	NBSKOY	0.0150	0.0800	
Chromium	0.0270	0.0200	0.0300	NBSKY	0.0150	0.0000	AvgSRM < 2 * LOD
Copper	0.5226	0.4160	0.6240	EPA LV	0.0150	0.0500	
Copper	4.0195	3.2000	4.8000	NBSKOY	0.0150	0.0500	
Copper	0.0465	0.0400	0.0600	NBSKY	0.0150	-0.7000	
Iron	2.0335	1.6648	2.4972	EPA LV	0.1500	-0.2300	
Iron	18.7604	16.0000	24.0000	NBSKOY	0.1500	-0.6200	
Iron	0.4835	0.4000	0.6000	NBSKY	0.1500	-0.3300	
Lead	4.8857	3.9680	5.9520	EPA LV	0.0150	-0.1500	
Lead	3.9315	3.2000	4.8000	NBSKOY	0.0150	-0.1700	
Lead	0.0491	0.0400	0.0600	NBSKY	0.0150	-0.1800	
Magnesium	18.1361	16.0000	24.0000	NBSKOY	0.0000	-0.9300	
Manganese	0.5057	0.4032	0.6048	EPA LV	0.0100	0.0300	
Manganese	4.2079	3.2000	4.8000	NBSKOY	0.0100	0.5200	
Manganese	0.1026	0.0800	0.1200	NBSKY	0.0100	0.2600	
Molybdenum	1.5347	1.6000	2.4000	NBSKOY	0.0008	-2.3300	
Nickel	0.4926	0.3880	0.5820	EPA LV	0.0100	0.1600	
Nickel	4.3270	3.2000	4.8000	NBSKOY	0.0100	0.8200	
Nickel	0.0454	0.0400	0.0600	NBSKY	0.0100	-0.9200	
Silver	1.6865	1.6000	2.4000	NBSKOY	0.0000	-1.5700	
Strontium	2.0155	1.6000	2.4000	NBSKOY	0.0000	0.0800	
Thallium	4.0694	3.2000	4.8000	NBSKOY	0.0500	0.1700	
Thallium	4.4291	4.0000	6.0000	NBSKY	0.0500	-1.1400	
Tin	2.3546	3.2000	4.8000	NBSKOY	0.0300	-4.1100	
Tin	0.0863	0.0800	0.1200	NBSKY	0.0300	-1.3700	
Vanadium	1.8908	1.6000	2.4000	NBSKOY	0.0000	-0.5500	
Zinc	2.7600	2.3360	3.5040	EPA LV	0.0300	-0.5500	
Zinc	3.9131	3.2000	4.8000	NBSKOY	0.0300	-0.2200	
Zinc	0.0556	0.0800	0.1200	NBSKY	0.0300	0.0000	AvgSRM < 2 * LOD

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Arsenic	0.0500	0.0376	0.0564	EPA LV	0.0030	0.6400
Arsenic	0.0395	40.0000	60.0000	NBSKOY	0.0030	-9.9900
Mercury	0.0050	-0.9751	0.9849	EPA LV	0.0002	0.0002
Mercury	0.0040	0.0039	0.0059	NBSKOY	0.0002	-1.8000
Selenium	0.0940	0.0832	0.1248	EPA LV	0.0025	-0.9600
Selenium	0.0500	0.0400	0.0600	NBSKOY	0.0025	0.0000

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Aluminum	1.6800	1.6000	2.4000	EPA LV	0.0500	-1.6000
Aluminum	20.0543	16.0000	24.0000	NBSKOY	0.0500	0.0300
Antimony	1.5723	3.2000	4.8000	NBSKOY	0.0030	-6.0700
Barium	1.9940	1.6000	2.4000	NBSKOY	0.0000	-0.0300
Beryllium	0.5090	0.4008	0.6012	EPA LV	0.0005	0.1600
Beryllium	2.1210	1.6000	2.4000	NBSKOY	0.0005	0.6100
Boron	1.8623	1.6000	2.4000	NBSKOY	0.0000	-0.6900
Cadmium	0.4340	0.3936	0.5904	EPA LV	0.0010	-1.1800
Cadmium	2.0120	1.6000	2.4000	NBSKOY	0.0010	0.0600
Chromium	0.4790	0.4024	0.6036	EPA LV	0.0150	-0.4800
Chromium	2.0110	1.6000	2.4000	NBSKOY	0.0150	0.0600
Copper	0.5180	0.4160	0.6240	EPA LV	0.0150	-0.0400
Copper	4.0207	3.2000	4.8000	NBSKOY	0.0150	0.0500
Iron	1.8780	1.6648	2.4972	EPA LV	0.1500	-0.9800
Iron	19.0457	16.0000	24.0000	NBSKOY	0.1500	-0.4800
Lead	3.9690	3.9680	5.9520	EPA LV	0.0150	-2.0000
Lead	3.9300	3.2000	4.8000	NBSKOY	0.0150	-0.1800
Magnesium	18.4253	16.0000	24.0000	NBSKOY	0.0000	-0.7900
Manganese	0.3560	0.4032	0.6048	EPA LV	0.0100	-2.9400
Manganese	4.2380	3.2000	4.8000	NBSKOY	0.0100	0.6000
Molybdenum	1.6197	1.6000	2.4000	NBSKOY	0.0000	-1.9000
Nickel	0.4490	0.3880	0.5820	EPA LV	0.0100	-0.7400
Nickel	4.3203	3.2000	4.8000	NBSKOY	0.0100	0.8000
Silver	1.7553	1.6000	2.4000	NBSKOY	0.0000	-1.2200
Strontium	2.0067	1.6000	2.4000	NBSKOY	0.0000	0.0300
Thallium	4.2123	3.2000	4.8000	NBSKOY	0.0500	0.5300
Tin	2.6420	3.2000	4.8000	NBSKOY	0.0300	-3.4000
Vanadium	1.9140	1.6000	2.4000	NBSKOY	0.0000	-0.4300
Zinc	2.2340	2.3360	3.5040	EPA LV	0.0300	-2.3500
Zinc	3.9603	3.2000	4.8000	NBSKOY	0.0300	-0.1000

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score	Comments
		Low SRM	Hi SRM				
*****					0.0000	0.0000	No Ref. Val.