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U.S. Department of Interior

May 31, 1993

EXECUTIVE SUMMARY

This study was conducted by the U.S. Fish and Wildlife Service during 1987 and 1988 on Selawik National Wildlife Refuge (Refuge). The objectives were to monitor water quality and concentrations of trace elements in water, stream sediments, and fish; evaluate impacts of heavy metal contamination and water quality degradation on Refuge water, sediment, and fish tissue due to placer mining; and make recommendations for future monitoring to develop baseline data. Samples were collected from Klery Creek, an area with gold mining activity upstream of the Refuge, and five sites within the Refuge near the Refuge boundaries with no mining nearby.

Mineral deposits of many types have been located in the upper Kobuk River valley, north of the Refuge. These include numerous copper, gold, and lead deposits. In addition, occurrences of antimony, chromite, cobalt, iron, nickel, and silver have been identified. Extraction of these resources could affect fish and wildlife resources of the Refuge, which are downstream of these areas.

Water quality characteristics of streams sampled during this study are typical of pristine calcium-magnesium bicarbonate systems. These characteristics include neutral to slightly basic pH, low conductivity, low to moderate hardness, and low to moderate alkalinity. Alkalinity, hardness, conductivity, and pH data at the seven sample sites can be divided into two groups: those at sites 1 (Kugarak River), 2 (Selawik River), and 3 (Tagagawik River); and two sites each on the Kobuk River and Klery Creek. Water quality at Sites 1, 2, and 3 appears to be determined by wetland/lacustrine inputs in the vicinity of the sample sites. Lower values of pH at these sites reflect the acidic conditions of peat marshes and lakes. This, combined with the low hardness and alkalinities at these sites, may increase the mobility of metals and contamination in aquatic organisms. The surficial geologies of Klery Creek (Sites 7 and 8) and the Squirrel River, into which it drains, are primarily marble and limestone, respectively. Water quality data from Sites 6 (Kobuk River below confluence with Squirrel River), 7, and 8 reflect the calcium carbonate nature of these bedrock materials.

Cadmium was detected at Sites 1, 2, 3, and 4 (Kobuk River above confluence with Squirrel River) in total water samples and was present in concentrations exceeding both the chronic and acute Environmental Protection Agency (EPA) Water Quality Criteria (WQC) (EPA 1986) at Sites 1 (0.004 mg/L), 2 (0.004 mg/L), and 3 (0.002 mg/L). Mean total recoverable and mean dissolved cadmium concentrations at Site 1 (0.004 and 0.002 mg/L, respectively) also exceeded the both the chronic and acute WQC. Dissolved copper concentrations exceeded both the chronic and acute WQC at Sites 1 (0.020 mg/L), 2 (0.029 mg/L), 3 (0.020 mg/L), and 4 (0.017 mg/L). Although copper and chromium concentrations at site 4 exceeded the WQC during 1987, neither metal concentration was elevated during 1988. The concentrations of copper, chromium, and cadmium in this study were less than 10 times the limit of detection and should, therefore, be considered semi-quantitative, and not cause for concern at this time. Further sampling should be conducted to verify these data.

During 1988, total mean iron concentrations in water at Site 6 (1.660 mg/L) and mean lead concentrations at Site 7 (0.028 mg/L) exceeded the WQC. High iron concentrations are not unusual in Alaska (Snyder-Conn et al. 1992a, b). Again, these concentrations were less than 10 times the limit of detection and should, therefore, be considered semi-quantitative.

Concentrations in 1987 sediment samples (Sites 1, 2, 3, and 4) for arsenic, beryllium, cadmium, copper, mercury, molybdenum, and zinc from this study are characteristic of uncontaminated sediments. Mean barium values from this study ranged up to 464 mg/kg which, in some areas,

would be considered very elevated; however, because other investigators have reported similar or higher values from northwestern Alaska, the values for barium in this study are considered background. Moderate to high levels of mercury were not present in sediment samples.

Cadmium was detected in at least one tissue each from 12 of 30 fish, and at each sample site except Site 7. Fish tissue samples were not collected at Sites 6 and 8. Cadmium concentrations in fish tissue ranged from <0.5 mg/kg to 1.0 mg/kg, the latter from a northern pike kidney.

Mercury was detected in each fish sampled regardless of location. Mercury concentrations in whole body, muscle, kidney, and liver samples from this study are within the range reported for uncontaminated conditions. Mean mercury concentrations in fish muscle tissue were higher at Site 4 than at any other site for both years; however, no correlation was found between the elevated mercury tissue levels at Site 4 and water and sediment data. Both grayling (Sites 2 and 7) and northern pike (Sites 1, 3, and 4) are highly migratory species and, even under ideal conditions, it is difficult to attribute tissue contaminant burdens in these species to conditions at specific locations.

Nickel was detected in 3 of 10 northern pike and 2 of 5 grayling with maximum concentrations of 25.7 mg/kg at Site 4 and 12.5 mg/kg at Site 7, respectively. These are considered to be high concentrations. Other investigators in this area of Alaska have found similar results, suggesting that nickel concentrations may be naturally elevated in northern Alaskan fish.

For both grayling and northern pike, no significant differences occurred between dorsal muscle and ventral muscle concentrations of mercury. This appears to indicate that analytical results from dorsal and ventral muscle tissue may be compared with no loss of consistency between samples for mercury.

No long-range effects of off-Refuge placer mining on Refuge water, sediments, and fish were found during this study.

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ACKNOWLEDGMENTS

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INTRODUCTION

Selawik National Wildlife Refuge in northwestern Alaska was created by the Alaska National Interest Lands Conservation Act of 1980 (ANILCA) and is comprised of approximately 849,858 ha (2.15 million acres) of land. The Selawik Refuge is east of Kotzebue Sound and is nearly bisected by the Arctic Circle (Figure 1). Included in the Refuge along the northern border are approximately 97,127 ha (240,000 acres) of Congressionally-designated wilderness. As part of the 1971 Alaska Native Claims Settlement Act, about 147,000 ha (363,000 acres), of the 1.29 million hectares (3.2 million acres) within the Selawik Refuge boundaries, have been conveyed to Alaska Native village corporations. In addition, applications for 581 Native allotments within the Refuge, totaling approximately 36,400 ha (90,000 acres), have been filed with the Bureau of Land Management. There are also 27,000 ha (67,000 acres) of private patented land within the Refuge (U.S. Fish and Wildlife Service [USFWS] 1987).

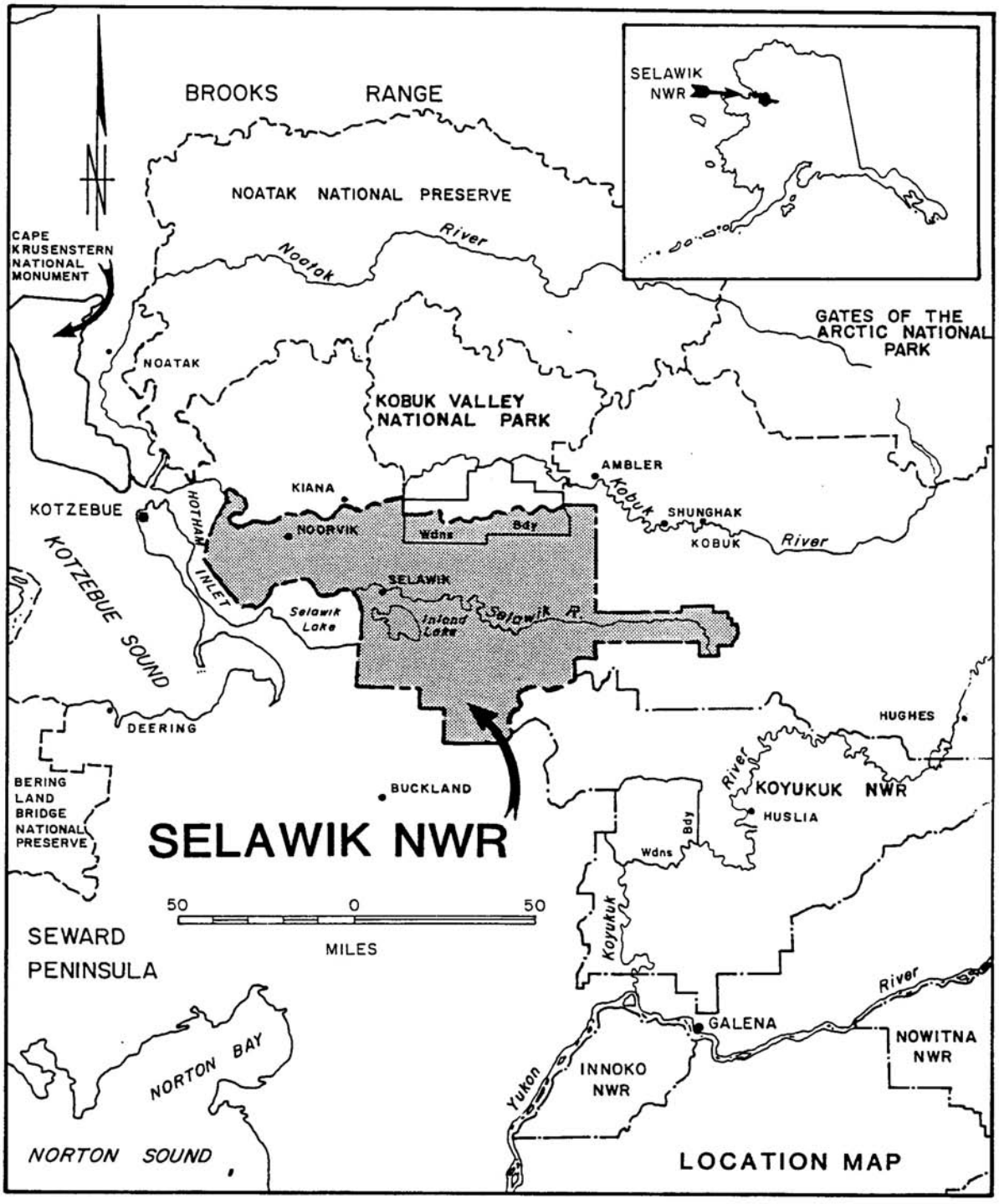
The vast majority of the Refuge lies within the Kobuk-Selawik Lowland (Wahrhaftig 1965). This lowland is characterized by broad river floodplains and delta/lowlands with numerous thaw lakes and ponds. The Kobuk-Selawik Lowland is a basin with uplands on three sides. The Selawik Refuge and adjacent lands include an extensive system of estuaries and lakes lying at the convergence of the Selawik and Kobuk river deltas. The Refuge is bordered, in part, on the north by the Kobuk Valley National Park and on the southeast by Koyukuk National Wildlife Refuge.

The purposes of Selawik Refuge are:

> (1) to conserve fish and wildlife populations and habitats in their natural diversity including, but not limited to, the Western Arctic Caribou Herd, waterfowl, shorebirds and other migratory birds, salmon, and sheefish;
>
> (2) to fulfill the international treaty obligations of the United States with respect to fish and wildlife, and their habitats;
>
> (3) to provide, in a manner consistent with the purposes set forth above, the opportunity for continued subsistence uses by local residents; and
>
> (4) to ensure, to the maximum extent practicable and in a manner consistent with the purposes set forth in (1) above, water quality and necessary water quantity within the Refuge (USFWS 1987).

Identified special resources of the Selawik Refuge include: the existing Selawik Wilderness; the Selawik River and its tributaries; the sheefish (*Stenodus leucichthys*) and whitefish (*Coregonus* spp.) spawning areas in the Selawik River; the Kobuk River delta; the wintering and spring staging grounds of the Western Arctic Caribou (*Rangifer tarandus*) Herd; the Selawik Wild River corridor; high-density moose (*Alces alces*) habitat; high-density

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



waterfowl breeding habitat; Selawik Hot Springs; and the sand dunes in the northeastern part of the Refuge (USFWS 1987).

Refuge lakes and rivers support both anadromous and freshwater fisheries, and include spawning grounds for sheefish, northern pike (*Esox lucius*), whitefish, grayling (*Thymallus arcticus*), Arctic char (*Salvelinus alpinus*), chum salmon (*Oncorhynchus keta*), and pink salmon (*O. gorbuscha*). In addition, Pacific herring (*Clupea harengus*) spawn in the coastal waters of Kotzebue Sound adjacent to the Selawik Refuge. Roughly 160 species of birds have been documented on the Selawik Refuge, and its wetlands support high densities of breeding waterfowl including birds from all four North American flyways.

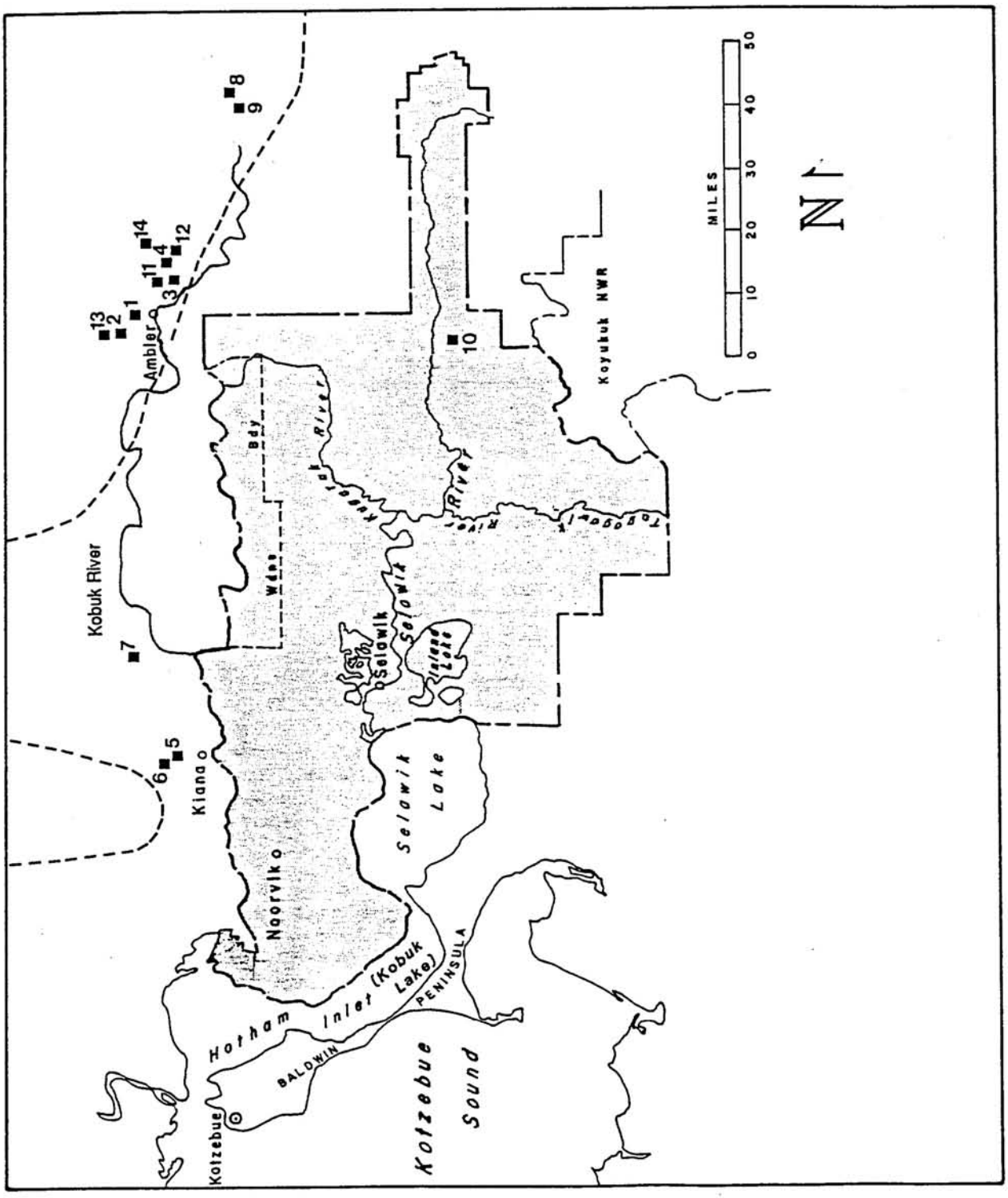
The Selawik Refuge lies in the northwest corner of the Yukon/Koyukuk Volcanic Province. No major mineral occurrences have been found within the Selawik Refuge (USFWS 1987). However, numerous mineral deposits of many types have been located north of the Refuge in the upper Kobuk and Squirrel river drainages (Figure 2). These include numerous lead deposits (Cobb 1984a), copper deposits in both the upper Kobuk River valley and the Squirrel River valley (Cobb 1984b), two occurrences of nickel and cobalt each (Cobb 1974a, b), one occurrence of zinc and iron each on the Shungnak River (Cobb 1964, 1975a), four occurrences of antimony (Cobb 1986), one occurrence of chromite near Kobuk (Cobb 1975b), and lode gold and silver in numerous places (Cobb 1984c). Many placer gold occurrences have been located on Klery Creek, in the Squirrel River drainage of the lower Kobuk River, and in the upper Kobuk River valley in the Shungnak River area (Cobb 1984d). Coal deposits are also located along the Kobuk River (USFWS 1987). The headwaters of the Kobuk River are underlain by a belt of granitic rocks containing deposits of copper, lead, molybdenum, silver, tin, tungsten, and zinc (U.S. Bureau of Mines [USBM] 1979).

Most surficial deposits in the interior lowland of the Refuge are glacial dirt, alluvium, and wind-blown material. The bulk of the material is till and outwash gravel covered with fine sand and silt. The sand dunes are composed of fine sand and silt (USFWS 1987).

Section 304(g)(2E) of ANILCA mandates identification and description of problems which may adversely affect Refuge fishery resources and wildlife populations. Commercial developments, including mining, on adjacent lands could adversely affect the Selawik Refuge's scenic, wilderness, air, and water resources, as well as restrict the opportunities for subsistence. Accessibility of and impacts to the Refuge could increase if nearby property is developed in the Ambler mining district, or other areas, complicating protection of Refuge resources. Placer gold or other types of mining near Refuge boundaries can potentially affect water quality, fish and wildlife populations, and their habitats. No known valid mining claims occur within the Refuge (USFWS 1987). However, numerous active mining claims exist in the Squirrel and upper Kobuk river drainages (Figure 3).

The earliest mining activity in the Selawik region was for gold in 1898, around Shungnak, east of the Refuge, in streams draining the Cosmos Hills (USFWS 1987). Gold mining has occurred off of the Refuge in portions of both the Kobuk and Selawik river drainages. In the Kobuk River drainage, gold mining has occurred intermittently at Klery Creek since 1909 and on adjacent Timber Creek, both in the Squirrel River drainage (Bundtzen et al. 1991), and on Westly Creek. The Shungnak district, which includes the Kobuk River drainage above the Ambler River, has several placer gold mining areas. Within the Selawik district, the only placer gold operation was on Shovel Creek, a tributary of Ingruksukruk Creek. An inactive exploration site and major copper, zinc, and cobalt lode deposit occurs in the upper Kobuk River drainage at Ruby Creek (Bornite) (USBM 1979; Bundtzen et al. 1991). In general, placer and lode mining activities for gold have increased dramatically in Alaska in recent decades (Alaska Department of Natural Resources 1982; U.S. Dept. Interior 1990).

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



Legend - Mineral Occurrences

1. Jade Hills (Nickel)
2. Jade Mountains (Copper, Lead)
3. Bismark Creek (Gold)
4. Aurora Mountain (Copper, Lead, Gold, Silver, Zinc)
   Iron Mountain (Iron)
   Ruby Creek (Cosmos Mountain) (Antimony, Cobalt, Copper, Iron, Lead, Zinc)
5. Peluck Creek (Gold)
   Baldwin Creek (Gold)
   Klery Creek (Gold)
   Gold Run Creek (Gold)
   Bear Creek (Gold)
   Central Creek (Gold)
6. Homestake Creek (Gold)
7. Salmon River (Copper)
8. Lynks (Gold)
9. Stockley Creek (Nickel)
   California Creek (Gold)
   Dahl Creek (Cadmium, Chromite, Copper, Gold, Silver)
10. Shovel Creek (Purcell Mountains) (Gold)
11. Smucker Creek (Antimony)
12. Bornite (Cobalt, Copper, Zinc)
13. Kalnick Area (Lead)
14. Horse Creek (Lead)
    Arctic (Lead)
    2 Unnamed Creeks (Lead)

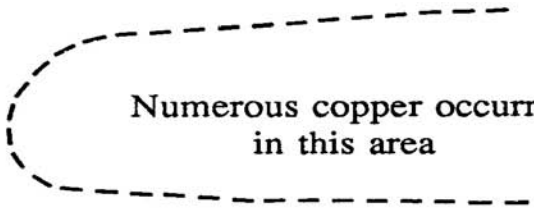
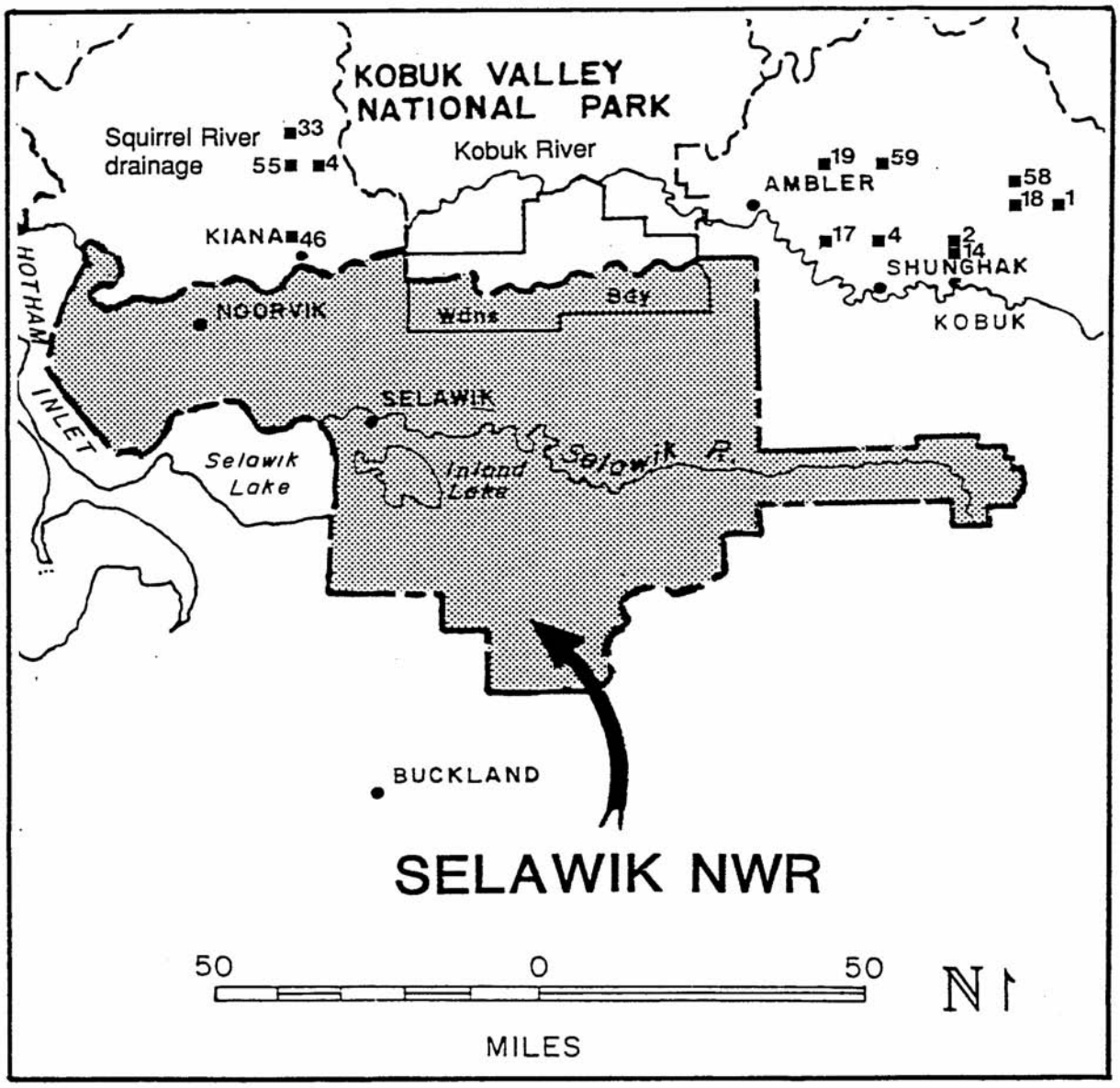


Figure 3. Location of active mining claims in drainages flowing into Selawik National Wildlife Refuge. Numbers indicate number of active mining claims in that township.



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

The objectives of this study were to:

1. Monitor water quality and concentrations of heavy metals in water, stream sediments, and fish from Klery Creek, and five sites within the Refuge, near the Refuge boundaries;

2. Evaluate existing impacts of heavy metal contamination and water quality degradation due to placer mining on Refuge water, sediment, and fish tissue; and

3. Make recommendations for future monitoring to develop baseline data to protect water quality, conserve fish and wildlife populations, and to protect subsistence use, consistent with Refuge goals.

METHODS AND MATERIALS

Study Sites

Samples were collected from seven sites, five on the Selawik Refuge and two off of the Refuge (Figure 4). Sample site descriptions are as follows:

Site 1, Located on the Kugarak River immediately downstream of its confluence with the Rabbit River, Sec. 9, T. 15 N., R. 3 E., Kateel River Meridian (KRM), 66°43'15"N., 150°15'00"W.

Site 2, Located on the Selawik River immediately downstream of Ingruksukruk Creek, Sec. 39, T. 13 N., R. 3 E., KRM, 66°29'38"N., 158°27'48"W.

Site 3, Located on the Tagagawik River, Sec. 1, T. 10 N., R. 2W., KRM, 66°17'45"N., 158°59'15"W.

Site 4, Located on the Kobuk River immediately downstream of its confluence with the Squirrel River, across the river from Okok Point, Sec.19, T. 18 N., R. 8 W., KRM, 66°56'35"N., 160°29'30"W.

Site 6, Located on the Kobuk River immediately upstream of its confluence with the Squirrel River, Sec. 15, T. 18 N., R. 7 W., KRM, 66°57'45"N., 160°11'20"W.

Site 7, Located on Klery Creek immediately downstream of the active mining operation, Sec. 16, T. 20 N., R. 8 E., KRM, 67°8'16"N., 160°26'00"W.

Site 8, Located on Klery Creek immediately upstream of the active mining operation, Sec. 26, T. 22 N., R. 8 E., KRM, 67°16'38"N., 160°23'33"W.

Collection Methods

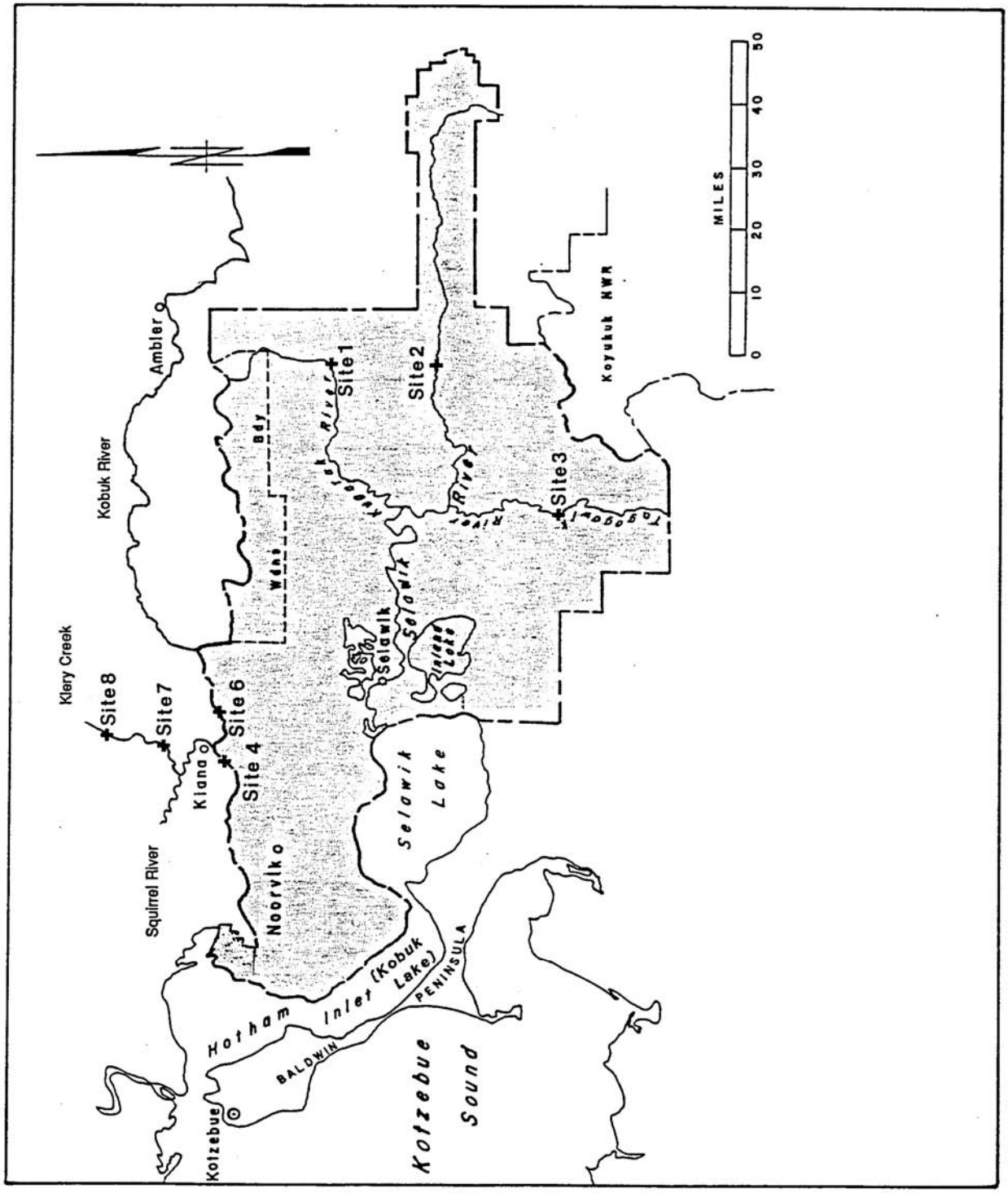
Samples were collected during 1987 and 1988. Four types of water samples were collected at each sample site: water quality, and dissolved, total recoverable (weak-acid digestion) and total (complete acid digestion) metals and metalloids. In addition, sediment and fish tissue samples were collected for metal and metalloid analysis. Samples were collected at Sites 1, 2, 3, and 4 during 1987 and Sites 4, 6, 7, and 8 during 1988.

Water

Water quality samples. During both 1987 and 1988, 1-L grab samples were taken in triplicate just below the water surface. During sampling, each sample bottle was extended into the current upstream of the collector to avoid contamination from resuspension of sediment by the collector. Samples were filled to the top of the bottle to minimize gaseous exchange. Each sample bottle was double-labelled immediately prior to collection and placed in a cooler with ice for transport to a field laboratory for analysis.

Samples were analyzed on the day of collection for pH, total alkalinity, total hardness, conductivity, turbidity, and settleable solids. Hardness and alkalinity determinations were made using a Hach Company digital titrator and Hach Company (1985) methods with colorimetric endpoints. Phenopthalein alkalinity was not observed in any sample. Conductivity was measured with a Hach Company DREL/5 conductivity meter with automatic temperature compensation. Conductivity

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



standards were used to check performance of this meter prior to each measurement series. Measurements of pH were made using a Hach One pH meter equipped with a combination electrode and automatic temperature compensation. Prior to each measurement series, two-buffer calibrations were performed using pH buffers accurate to ± 0.02 pH units which bracketed the pH of the samples. Low ionic strength buffers were used during 1988.

Three measures of solids in water were also made. Turbidity was measured using a Hach Company Portable Turbidity Meter Model 16800, calibrated with Gelex secondary standards for 1, 10, and 100 nephelometric turbidity units (NTU). Samples for total suspended solids analysis were collected, during 1987 only, and sent to a commercial laboratory for analysis. Total settleable solids were measured using the Imhoff Cone Method for 1-L samples (APHA et al. 1981). Settleable solids measured as ≤0.1 mL/L were recorded as "trace."

Trace element samples. Water samples for metals analysis were surface grab samples collected in triplicate in the same manner as the water quality samples. Unfiltered, acidified samples were collected for analysis of total metals and total recoverable metals, and filtered, acidified samples were collected for dissolved metals. Dissolved metal samples were filtered in the field using 0.8 µm disposable prefilters together with 0.45 µm disposable cellulose-acetate filters with Luerlock fittings fitted on disposable syringes. The volume of filtered samples was approximately 125 mL. Samples for total metals and total recoverable metals analysis were acidified with 2-mL HNO_3 (Ultrix). Samples for dissolved metals analysis were acidified with either 1-mL (1987) or 1.2-mL (1988) HNO_3 (Ultrix). All trace metal water samples were collected in acid-cleaned 500- or 250-mL high-density polyethylene I-Chem bottles. During 1988, for each replicate pair of total and total recoverable samples at each site, a single unfiltered sample was collected. This sample was split at the laboratory to represent both the total and total recoverable metals samples. Water samples were refrigerated as soon as possible after collection.

Sediment

Three sediment samples were collected from shore at each study site using a stainless steel strainer. Samples were transferred to new acid-cleaned 500-mL (1987) or 250-mL (1988) I-Chem polyethylene bottles with teflon-lined lids following field homogenization using a clean glass cylinder. Fine silt was sought for sampling in all cases. Each sample bottle was double-labelled immediately prior to collection and placed in a cooler with ice for transport to a freezer.

Fish Tissue

Fish were collected by angling from Refuge study sites in both 1987 and 1988. Five fish were collected at each sample site. Target fish species included adult Arctic grayling and northern pike. Samples were weighed with a Pesola scale to within 5 grams, and total and fork lengths were measured to the nearest millimeter. During 1987, whole fish samples were each stored in double ziplock bags. During 1988, liver, kidney and muscle samples were dissected from each fresh-caught fish >350 mm in length using stainless steel instruments and transferred to new 60-mL I-Chem bottles acid-precleaned for metals analysis. Fish ≤350 mm were stored in double ziplock bags. Each sample, in both 1987 and 1988, was double-labelled immediately following collection and placed in a cooler with ice for transport to a freezer.

Sample Handling and Labelling

Details of sample handling and labelling are presented in Appendices A and B. Briefly, sampling was conducted following a written study plan containing designated sample locations and types of samples to be collected at each site. At the time of collection, samples collected and other pertinent

data were recorded in a field notebook. A sample catalog was then prepared for each year of collection prior to submittal of samples to the analytical laboratory. The catalog contained a regional identifier for the sample batch; study objectives; background information summarizing types of samples, sample and preservation methods, and additional rationale for the study; instructions to the laboratory on analyses requested; identification of the detection limits sought; addresses of data recipients; and a tabulated summary of all samples including species, tissue matrix, location, collection date, weight, and other parameters.

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

Laboratory Analyses

Prior to analysis, each sediment sample was freeze-dried, sieved to remove large particles, and homogenized by grinding with a mortar and pestle. Fish tissues were also freeze-dried and homogenized using a food processor, followed by digestion and analysis. Fish collected during 1987 were dissected by the laboratory to obtain both dorsal and ventral muscle samples which were analyzed separately and compared to whole body samples of the same fish minus the liver, kidney and muscle samples. Fish collected during 1988 were either stored and analyzed as whole fish or dissected by the collectors in the field using stainless steel instruments. Dissections were of kidney, liver, and dorsal muscle tissues.

Samples for inductively-coupled argon plasma spectroscopy (ICP) analysis were digested with nitric acid for tissue; nitric and hydrochloric acids for water; and nitric, hydrochloric, and hydrofluoric acids for sediment. Tissue and sediment samples were digested for analysis of total metals. Samples for mercury analysis were digested with nitric acid according to the method of Monk (1961) and analyzed by cold vapor atomic absorption spectrophotometry. Samples for arsenic and selenium were digested using nitric acid and analyzed by flameless atomic absorption spectrophotometry using a graphite furnace. Samples for other metals were analyzed using ICP, with preconcentration for water and tissue samples prior to analysis.

Quality Assurance/Quality Control

Field Collections

All trace element samples were collected in new, precleaned I-Chem containers using protocols designed to reduce the potential of sample contamination. These included precautions to avoid direct contact between the sample container or sample and the collector or other sources of contamination.

Water quality sample containers were triple-rinsed in the river water to be sampled prior to sampling. Water quality measurements were all performed on the same day as collection with the exception of the suspended solids measurement, which was performed by a commercial analytical laboratory at a later date. Laboratory quality control procedures were followed during analysis of water quality samples. These included instrument calibrations or calibration checks prior to measurement of pH, conductivity, and turbidity; use of fresh reagents in titrations for hardness and alkalinity; and repeat analysis if a replicate sample deviated significantly from other measurements. Suspended solid measurements were also subject to performance checks using EPA check samples.

Sample locations and sample numbers were assigned prior to field sampling. All samples were labelled both on the lids and the bottles to reduce problems with label loss. Water samples were collected by direct surface grabs into the current. Samples were refrigerated as soon as possible after collection and shipped to the laboratory by air courier in coolers containing ice packs.

Sediment sampling followed water sampling and was performed using stainless steel, plastic, and glass equipment. All sample gear was triple-rinsed in river water at the sample site prior to sampling. Composite samples consisting of three to four grabs each constituted a replicate sample. During all phases of sediment collection, care was taken to avoid any contact between the sample and hands or footwear. Samples were frozen following collection and shipped to the laboratory in coolers with dry ice by overnight air courier.

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. The contract laboratory conducted dissections using carbon steel dissecting equipment and ultraclean conditions. Dorsal and ventral muscle from the midsection, above and below the lateral line, respectively, minus the skin, were collected from larger fish for analysis of trace elements. The whole fish minus these tissues and liver and kidney were also analyzed for trace elements. Smaller fish were analyzed as whole fish, including the viscera and gut contents. In 1988, dissections of dorsal muscle, liver and kidney were performed by the collector in the field. Dissections were performed with stainless steel and teflon dissection equipment on a clean metal-free surface, with new blades used on each tissue sample. Tissues were immediately placed in precleaned I-Chem containers and weighed on a tared balance to reduce contaminant exposure. Samples were shipped to the laboratory in coolers with ice or dry ice by overnight air courier. For both years, fish tissue samples were frozen and shipped to the laboratory in the same manner as sediment samples.

Laboratory Analyses

Two separate quality assurance/quality control (QA/QC) analyses were performed on the metals data: one by the Patuxent Analytical Control Facility (PACF), Laurel, Maryland, and one by Ecological Services, Fairbanks, Alaska. The PACF QA/QC analysis was based on measurements of overall laboratory performance and, to a lesser extent, data from the 1987 and 1988 Selawik Refuge sample sets. The QA/QC analysis by Ecological Services, Fairbanks was based solely on data contained within the 1987 and 1988 data sets. A description of the screening criteria to accept/reject analytical data, screening results, and the basis for rejection of certain analytical data, are contained in Appendices C and D. In summary, duplicate (split) samples, spiked samples, standard reference materials (SRM's), and blank data were used to evaluate data quality. Tables 1 and 2 identify acceptable analytical data sets for water, sediments, and fish tissue analyses based on duplicate, spike, SRM and blank criteria, and method limits of detection (LOD).

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

Concentrations of iron, nickel, and zinc in 1987 samples were higher for dissolved metals than for total metals. This unacceptable situation may be caused either by the addition of metals to the dissolved samples during filtration or analytical error. The 1987 and 1988 water samples for mercury were held longer than the maximum recommended holding time (APHA et al. 1989) and, as a result, these data were discarded.

Table 1. Acceptable data for metals in water and laboratory method detection limits (mg/L). 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).

Analyte	Method[a]	1987	1988
Aluminum	ICPP		
Arsenic	AA	All[b,c] 0.004	TM[d], DM[d] 0.003
Beryllium	ICPP	All[d] 0.002	TRM 0.0005
Cadmium	ICPP	All[d] 0.002	All[d] 0.001
Chromium	ICPP	TM, TRM[d] 0.003	TRM[d], DM[d] 0.015
Cobalt	ICPP		N/A[e]
Copper	ICPP	DM 0.004	TRM[d], DM[d] 0.015
Iron	ICPP	TM 0.015	TM[d], DM[d] 0.15
Lead	ICPP	TM[d], TRM[d] 0.012	TRM[d], DM[d] 0.015
Manganese	ICPP		TRM, DM[d] 0.01
Mercury	AA	TRM[d], DM .0004	All[f] 0.0002
Nickel	ICPP		All[d] 0.01
Selenium	AA	N/A	All[g] 0.0025
Thallium	ICPP	N/A	All[d] 0.05
Tin	ICPP		TM[d], TRM[d] 0.03
Zinc	ICPP		TRM[d], DM[d] 0.03

[a] ICPP = Inductively-coupled argon plasma spectroscopy analysis with preconcentration; AA = atomic absorption spectrophotometry.
[b] TM = total metals analysis; TRM = total recoverable metals analysis; DM = dissolved metals analysis; All = TM, TRM, and DM.
[c] DM Qualitative Data; [d] Qualitative Data.
[e] No analysis for this analyte; [f] TRM Qualitative Data.
[g] TM and DM Qualitative Data.

Table 2. Acceptable data for metals in sediments and fish tissues showing laboratory method detection limits (mg/kg dry weight). 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 denote where either duplicate had a value less than twice the limit of detection (precision not estimated).

		SEDIMENT		TISSUE	
Analyte	Method[a]	1987	1988	1987	1988
Aluminum	ICP/ICPP	30			
Arsenic	AA	0.4		0.4	
Beryllium	ICP/ICPP	1.0		0.30	0.2
Cadmium	ICP/ICPP	1.0		0.03	0.5
Chromium	ICP/ICPP				
Cobalt	ICP/ICPP	N/A[b]	N/A		N/A
Copper	ICP/ICPP	5.0			
Iron	ICP/ICPP			5.0	
Lead	ICP/ICPP				3.0
Manganese	ICP/ICPP				
Mercury	AA	0.02	0.1	0.02	0.1
Nickel	ICP/ICPP				2.0
Selenium	AA	14		N/A	
Thallium	ICP/ICPP				10
Tin	ICP/ICPP				
Vanadium	ICP/ICPP	8.8		N/A	N/A
Zinc	ICP/ICPP	7.0			

[a] ICP/ICPP = Inductively Coupled Argon Plasma spectroscopy analysis for all sediment and tissue for 1988; ICP with preconcentration for 1987 tissue; AA = atomic absorption spectrophotometry.
[b] No analysis for this analyte.

Statistical Analyses

Data sets subjected to statistical analysis were transformed from the DBase IV data management system to Lotus 3.0, where files were reformatted, missing values replaced with -99, and values below the detection limit replaced by one-half the detection limit. Data sets with a majority of nondetected values were not subjected to statistical analysis. Statistical analyses were performed using SPSS/PC+ statistical software.

In virtually all cases, sample sizes among sample sites were similar, based on the sampling 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. Data set means were compared using the one-way analysis of variance (ANOVA) and the Student-t test. Some data sets contained parameters which did not meet the requirements for use of parametric statistics, i.e., distributions were not normal or variances were not homogenous. In these instances, the Kruskal-Wallis test for three or more samples was used. Results of parametric and complementary nonparametric tests were then compared. Significant differences ($P < 0.05$) or highly significant differences ($P < 0.01$) were only reported when the results agreed. The Scheffe' multiple range test, a conservative parametric test for pairwise comparisons of means (Sokol and Rohlf 1981), was performed to identify differences among specific data sets.

Correlations were examined using Pearson product-moment correlations for pairs of variables (Sokol and Rohlf 1981). Correlations are expressed as significant, $P < 0.01$, or highly significant, $P < 0.001$. The effects of metals contamination on the length:weight ratio of fish was determined using multiple regression analysis.

RESULTS

Water Quality

Water quality data for 1987 and 1988 are presented in Table 3. Significant differences occurred in conductivity, total hardness, total alkalinity, pH, and turbidity among sites within each sample year (Table 3). The mean turbidity value at Site 8 (Upper Klery Creek) was more than an order of magnitude greater than at the next highest site. Trace settleable solids were measured at Sites 1, 2, 3, 4, and 6. No settleable solids were observed at Sites 7 and 8.

Site 4 (Kobuk River below the Squirrel River) was the only site sampled during both years. The values for pH, conductivity, total alkalinity, total hardness and turbidity were significantly different at this site between years, but absolute differences were not great. In addition, the values of hardness, alkalinity, and conductivity at this site were the highest values measured for these parameters at any site (Table 3).

Trace Elements

Water

Total Metals. 1987 - QA/QC screening indicated that arsenic, beryllium, cadmium, chromium, iron, and lead data were acceptable from 1987 samples (Table 4). Arsenic and lead were not detected in any samples. Beryllium was detected in less than one-half of the samples at or near the LOD (0.002 mg/L). Cadmium was detected in all but three samples; however, all concentrations were near the limit of detection and these data should be considered semi-quantitative. Chromium and iron were detected in all samples with concentrations ranging from 0.006 to 0.014 mg/L, and from 0.234 to 0.757 mg/L, respectively.

Examination of 1987 total metals in water data indicated only one significant difference in metal concentrations among sample sites. Iron concentrations at Site 1 (Kugarak River) were significantly greater than those at Site 3 (Tagagawik River) ($F_{3,8} = 4.98$, $P = .03$). Analysis of the means of these data using the Pearson correlation test showed no correlations among metals. There was only one significant correlation between a metal and a water quality parameter. Iron was positively correlated with turbidity ($r^2 = 0.76$, $df = 11$, $P < 0.01$).

1988 - QA/QC screening indicated that arsenic, cadmium, iron, nickel, selenium, tin, thallium, and zinc data were acceptable from 1988 samples; of these, only iron was detected. The arsenic and selenium analyses had undesirably high limits of detection of 3.0 mg/L and 2.0 mg/L, respectively, well above EPA Water Quality Criteria for protection of freshwater life (WQC) (EPA 1986). Iron was detected in only four samples, including three samples at Site 6 which had a mean iron concentration of 1.66 mg/L. Because all concentrations were near the limit of detection, iron data should be considered semi-quantitative.

Total Recoverable Metals. 1987 - QA/QC screening indicated that arsenic, beryllium, cadmium, chromium, and lead data were acceptable from 1987 samples (Table 5). Lead was not detected in any sample. Arsenic and beryllium were detected in only 3 of 12 samples and all at the limit of detection. Cadmium and chromium were detected in almost all samples; however, because all concentrations of these elements were near the limit of detection, these data should be considered semi-quantitative. Examination of the data for cadmium and chromium using the ANOVA test to examine differences among sample sites, and Pearson correlations to examine correlations with water quality parameters, revealed no significant relationships.

Table 3. Water quality data and Scheffe' groupings expressing significant differences of water quality parameters at Selawik National Wildlife Refuge, Alaska, 1987 - 1988. Each numeric value is the mean of three replicate analyses. Sample sites having different superscript letters for a given parameter were significantly different ($P < 0.05$) within each year.

Sample Site	Collection Date	Conductivity µS/cm	pH	Total Hardness (mg/L)	Total Alkalinity (mg/L)	Settleable Solids (mg/L)	Suspended Solids (mg/L)[1]	Turbidity (NTU)
1	9/9/87	60^{A}	7.3^{A}	35.8^{A}	25.9^{A}	trace	4.1^{A}	4.2^{B}
2	9/10/87	69^{A}	7.1^{A}	34.7^{A}	29.5^{A}	trace	1.8^{A}	1.8^{A}
3	9/10/87	108^{B}	7.3^{A}	54.5^{B}	45.7^{B}	trace	1.6^{A}	1.9^{A}
4	9/9/87	162^{C}	8.0^{B}	81.5^{C}	71.3^{C}	trace	16.3^{B}	3.5^{AB}
4	7/11/88	189^{A}	8.2^{A}	105.3^{A}	82.6^{A}	trace	-	0.3^{A}
6	7/11/88	174^{B}	8.2^{A}	89.0^{AB}	79.0^{B}	trace	-	0.1^{A}
7	7/10/88	158^{C}	8.4^{B}	82.3^{B}	71.8^{C}	0	-	1.7^{B}
8	7/10/88	159^{C}	8.1^{C}	82.7^{B}	69.1^{C}	0	-	49.9^{C}

[1] Not measured.

Table 4. Total metal concentrations (mg/L) in water from Selawik National Wildlife Refuge, Alaska, 1987.

Site	Rep.	Date	Be	Cd	Cr	Fe
1	A	09/10/87	<0.002	0.005	0.010	0.579
1	B	09/10/87	0.003	0.003	0.012	0.970
1	C	09/10/87	<0.002	0.003	0.007	0.721
Mean[a]				0.004	0.010	0.757
2	A	09/10/87	<0.002	0.003	0.012	0.533
2	B	09/10/87	<0.002	0.008	0.011	0.452
2	C	09/10/87	0.003	<0.002	0.007	0.526
Mean				0.006	0.010	0.504
3	A	09/11/87	0.002	0.002	0.006	0.418
3	B	09/11/87	<0.002	0.002	0.008	0.481
3	C	09/11/87	0.006	0.002	0.008	0.234
Mean			0.003	0.002	0.007	0.378
4	A	09/11/87	<0.002	0.002	0.011	0.465
4	B	09/11/87	<0.002	<0.002	0.011	0.523
4	C	09/11/87	0.002	<0.002	0.014	0.566
Mean			-	-	0.012	0.518

[a] Where concentrations of two replicates were < Limit of Detection (LOD), sample means were not calculated; when only one replicate was < LOD, a value of one-half of the LOD was used for that replicate in calculation of the mean. LODs (mg/L) were as follows: Be 0.002, Cd 0.002, Cr 0.003, and Fe 0.015.

1988 - QA/QC screening indicated that arsenic, cadmium, chromium, copper, lead, manganese, nickel, tin, selenium, thallium, and zinc data were acceptable from 1988 samples. Only lead and manganese were detected in these samples and then in only two and six samples, respectively. The mean lead concentration at Site 7 was 0.028 mg/L. Mean manganese concentrations at Sites 4 and 6 were 0.038 mg/L and 0.056 mg/L, respectively. Again, the analyses for arsenic and selenium had undesirably high limits of detection.

Dissolved Metals. 1987 - QA/QC screening indicated that arsenic, beryllium, cadmium, and copper data were acceptable from 1987 samples (Table 6). Arsenic and beryllium were not detected in any sample. Cadmium was detected in two samples at the LOD. Nickel was detected in 6 of 12 samples, however, because all concentrations were near the LOD these data should be considered semi-quantitative. Zinc was detected in all samples in concentrations ranging from 0.044 to 0.079 mg/L. Examination of the data for copper using the ANOVA test among sample sites, and Pearson correlations among dissolved metal and water quality parameters, showed no significant relationships.

1988 - QA/QC screening indicated that arsenic, cadmium, chromium, copper, iron, lead, manganese, nickel, selenium, thallium, and zinc data were acceptable from 1988 samples. Only lead and manganese were detected from these samples; however, because all concentrations were near the LOD, these data should be considered semi-quantitative. The mean lead concentration at Site 4 was 0.034 mg/L. Dissolved lead was detected at Sites 6 and 8 in this study; however, because lead was not detected in either the total or total recoverable analyses at these sites, contamination or analytical error is suspected in the dissolved samples. The analyses for arsenic and selenium had undesirably high limits of detection.

Sediment

All sediment samples were analyzed for total metals, i.e., with a strong acid digestion. QA/QC screening indicated that aluminum, arsenic, barium, beryllium, cadmium, copper, mercury, molybdenum, selenium, silver, vanadium and zinc data were acceptable from 1987 samples. Cadmium, molybdenum, silver, and selenium were not detected in any sample, and beryllium was detected in only two samples (Table 7). Aluminum, arsenic, barium, vanadium, and zinc were detected in every sample. Mercury was detected in one-half of the samples, but always near the limit of detection (Table 7). During 1988, only mercury data survived QA/QC screening and all concentrations were < LOD (0.02 mg/kg).

Aluminum, arsenic, and mercury concentrations in 1987 did not differ significantly among sites. All other mean metal concentrations differed significantly between at least two sites (Table 8). Analysis of metals concentrations and water quality data using Pearson correlations yielded several significant correlations. Vanadium concentrations were correlated with copper ($r^2 = 0.89$, df = 11, $P < 0.001$) and zinc ($r^2 = 0.74$, df = 11, $P < 0.01$) concentrations. Turbidity levels were positively correlated with arsenic concentrations ($r^2 = 0.74$, df = 11, $P < 0.01$). However, differences in arsenic among sites were not large.

Fish Tissue

1987. QA/QC screening indicated that arsenic, beryllium, cadmium, iron, and mercury data were acceptable from samples collected in 1987 (Tables 9 and 10). Sixty samples from 20 fish were analyzed. Arsenic and beryllium were detected in northern pike only, in three and six samples, respectively. Cadmium was detected in 12 samples from northern pike and Arctic grayling. Iron and mercury were detected in each sample in

Table 5. Total recoverable metal concentrations (mg/L) in water from Selawik National Wildlife Refuge, Alaska, 1987.

Site	Rep.	Date	As	Be	Cd	Cr
1	A	09/10/87	<0.004	<0.002	0.003	<0.003
1	B	09/10/87	<0.004	<0.002	0.002	0.006
1	C	09/10/87	<0.004	<0.002	0.007	0.009
Mean[a]					0.004	0.005
2	A	09/10/87	<0.004	<0.002	0.002	0.004
2	B	09/10/87	<0.004	<0.002	0.002	0.011
2	C	09/10/87	<0.004	<0.002	0.002	0.005
Mean					0.002	0.007
3	A	09/11/87	<0.004	<0.002	0.002	0.008
3	B	09/11/87	<0.004	0.002	<0.002	0.006
3	C	09/11/87	<0.004	0.002	<0.002	0.011
Mean				0.002		0.008
4	A	09/11/87	0.004	<0.002	0.002	0.010
4	B	09/11/87	0.004	0.003	0.003	0.006
4	C	09/11/87	0.004	<0.002	0.002	0.007
Mean			0.004		0.002	0.008

[a] Where concentrations of two or three replicates were < LOD, means were not calculated; when only one replicate was < LOD, a value of one-half of the LOD was used for that replicate in calculation of the mean. LODs were as follows: As 0.004, Be 0.002, Cd 0.002, and Cr 0.003.

Table 6. Total dissolved metal concentrations (mg/L) in water from Selawik National Wildlife Refuge, Alaska, 1987.

Site	Rep.	Date	Cd	Cu
1	A	09/10/87	<0.002	0.019
1	B	09/10/87	<0.002	0.025
1	C	09/10/87	<0.002	0.015
Mean[a]				0.020
2	A	09/10/87	<0.002	0.039
2	B	09/10/87	<0.002	0.023
2	C	09/10/87	<0.002	0.025
Mean				0.029
3	A	09/11/87	0.002	0.021
3	B	09/11/87	0.002	0.022
3	C	09/11/87	<0.002	0.018
Mean			0.002	0.020
4	A	09/11/87	<0.002	0.025
4	B	09/11/87	<0.002	0.021
4	C	09/11/87	<0.002	0.004
Mean				0.017

[a] Where concentrations of two or three replicates were < LOD, means were not calculated; when only one replicate was < LOD, a value of one-half of the LOD was used for that replicate in calculation of the mean. LODs (mg/L) were as follows: Cd 0.002, Cu 0.004.

Table 7. Metal concentrations (mg/kg dry weight) in sediment from Selawik National Wildlife Refuge, Alaska, 1987.

Site	Rep.	Date	Al	As	Ba	Be	Cu	Hg	V	Zn
1	A	09/10/87	19700	4.53	204.0	<1.0	<5.0	0.02	26.8	44.3
1	B	09/10/87	26700	5.09	217.0	<1.0	5.00	<0.02	37.3	37.5
1	C	09/10/87	11200	2.24	74.5	<1.0	2.95	0.03	27.2	28.1
Mean[a]			19200	3.95	165.2		3.98	0.03	30.4	36.6
2	A	09/10/87	37500	2.84	382.0	1.31	8.82	0.03	64.0	52.9
2	B	09/10/87	37800	4.20	382.0	<1.0	13.70	0.04	71.0	56.0
2	C	09/10/87	16900	2.91	296.0	<1.0	9.50	<0.02	55.3	43.6
Mean			30733	3.32	353.3		10.67	0.04	63.4	50.8
3	A	09/11/87	15200	2.64	491.0	<1.0	9.49	0.02	42.4	37.0
3	B	09/11/87	38800	2.58	457.0	<1.0	5.66	0.03	41.8	33.4
3	C	09/11/87	31600	2.04	446.0	<1.0	6.06	<0.02	41.3	25.9
Mean			28533	2.42	464.7		7.07	0.03	41.8	32.1
4	A	09/11/87	16800	3.30	66.4	<1.0	7.11	<0.02	56.0	48.5
4	B	09/11/87	4990	4.08	69.0	<1.0	7.90	<0.02	56.3	62.0
4	C	09/11/87	36400	6.34	339.0	1.16	9.60	<0.02	59.0	58.3
Mean			19397	4.57	158.1		8.20		57.1	56.3

[a] Where concentrations of two or three replicates were < LOD, means were not calculated; when only one replicate was < LOD, a value of one-half of the LOD was used for that replicate in calculation of the mean. LODs (mg/kg dry weight) were as follows: Al 30, As 1.0, Ba 1.2, Be 1.0, Cu 5.0, Hg 0.02, V 8.8, and Zn 7.0.

Table 8. Scheffe' groupings expressing significant differences of mean metal concentrations at four sediment sample sites collected at Selawik National Wildlife Refuge, Alaska, 1987. Sample sites containing different letters for a specific metal had significantly different ($P < 0.05$) metal concentrations.

Sample Site	Ba	Cu	Se	V	Zn
1	A	A	A	A	A
2	AB	B	B	B	AB
3	B	AB	B	A	A
4	A	AB	A	B	B

concentrations ranging from 7.27 to 135.00 mg/kg, and from 0.12 to 1.84 mg/kg, respectively.

Examination of northern pike and Arctic grayling whole body analyses for cadmium, iron, and mercury, using the ANOVA test, showed several significant differences in mean metal concentrations among sample sites. Mean iron concentrations in whole body samples at Site 2 (Selawik River), 75.9 mg/kg in Arctic grayling, were significantly higher than those at Site 1 (Kugarak River), 27.0 mg/kg in northern pike, indicating either a species or site difference. Similarly, whole body mercury concentrations of northern pike at Site 4 (Kobuk River below Squirrel River), 0.75 mg/kg, were significantly higher than those of Arctic grayling at Site 2 (Selawik River), 0.14 mg/kg. Mercury concentrations in muscle at Site 4 were significantly higher than those at Sites 1 and 2. There were no significant correlations between metal concentrations in fish tissue and body weight or length. Mean metals concentrations in northern pike and Arctic grayling whole body analyses were not significantly correlated with water quality parameters, except that iron concentrations in northern pike and pH were positively correlated ($r^2 = 0.60$, $df = 14$, $P < 0.01$). Mean metals concentrations in muscle tissue were not significantly correlated with water quality parameters. Iron concentrations of Arctic grayling and northern pike muscle were not significantly different, but mercury concentrations were significantly different ($t = -5.61$, $df = 38$, $P < 0.01$) with northern pike having higher mercury concentrations. No significant correlations were found between iron and mercury concentrations in fish muscle and body weight or length.

Mercury concentrations in dorsal and ventral muscle of northern pike were not significantly different; however, ventral muscle iron concentrations were somewhat greater than dorsal muscle concentrations ($t = 1.85$, $df = 15$, $P = 0.08$). Iron concentrations in northern pike muscle, with dorsal and ventral muscle data combined, were significantly lower than in whole body samples ($t = 2.79$, $df = 35$, $P < 0.01$). Mercury concentrations in dorsal and ventral muscle of Arctic grayling were not significantly different, but iron concentrations were significantly greater in ventral muscle than in dorsal muscle ($t = 2.63$, $df = 7$, $P < 0.05$). Iron concentrations were significantly greater in Arctic grayling whole body samples than in muscle samples ($t = 3.76$, $df = 4$, $P < 0.05$); however, mercury concentrations were significantly greater in muscle samples ($t = 4.56$, $df = 12.18$, $P < 0.01$) than in whole body samples.

Table 9. Tissue metal concentrations (mg/kg dry weight), total length (mm), and weight (gm) in northern pike (*Esox lucius)* tissue from Selawik National Wildlife Refuge, Alaska, 1987.

Site	Tissue[a]	Date	As	Be	Cd	Fe	Hg	TL[b]	WT[c]
1	VM	08/25/87	<0.4	<0.30	<0.03	11.3	0.31	550	1080
1	VM	08/26/87	<0.4	<0.30	0.34	28.9	0.44	510	815
1	VM	08/26/87	<0.4	<0.30	<0.03	18.0	0.22	521	760
1	VM	08/26/87	<0.4	<0.30	<0.03	135.0	0.48	583	1270
1	VM	08/26/87	<0.4	<0.30	<0.03	20.0	0.57	649	1600
Mean[d]						42.6	0.40	562	1105
1	DM	08/25/87	<0.4	<0.30	<0.03	12.3	0.41	550	1080
1	DM	08/26/87	<0.4	<0.30	<0.03	20.2	0.33	510	815
1	DM	08/26/87	<0.4	<0.30	<0.03	14.0	0.18	521	760
1	DM	08/26/87	<0.4	<0.30	<0.03	9.8	0.69	583	1270
1	DM	08/26/87	<0.4	<0.30	<0.03	12.5	0.78	649	1600
Mean						13.8	0.48	563	1105
1	W	08/25/87	<0.4	<0.30	<0.03	15.9	0.37	550	1080
1	W	08/26/87	<0.4	<0.30	<0.03	32.9	0.16	510	815
1	W	08/26/87	<0.4	0.83	<0.03	35.5	0.24	521	760
1	W	08/26/87	<0.4	<0.30	<0.03	17.4	0.38	583	1270
1	W	08/26/87	<0.4	<0.30	<0.03	33.5	0.36	649	1600
Mean						27.0	0.30	563	1105
3	VM	08/27/87	<0.4	<0.30	<0.03	22.0	0.53	422	460
3	VM	08/28/87	<0.4	<0.30	0.45	41.3	0.63	445	530
3	VM	08/28/87	<0.4	<0.30	0.32	19.3	1.75	542	950
3	VM	08/28/87	<0.4	0.35	<0.03	13.5	0.65	555	1150
3	VM	08/28/87	<0.4	<0.30	<0.03	30.6	0.54	515	760
Mean						25.3	0.82	496	770
3	DM	08/27/87	<0.4	<0.30	<0.03	16.7	0.51	422	460
3	DM	08/28/87	<0.4	<0.30	<0.03	13.8	0.62	445	530
3	DM	08/28/87	<0.4	<0.30	<0.03	22.2	1.84	542	950
3	DM	08/28/87	<0.4	<0.30	<0.03	7.3	0.60	555	1150
3	DM	08/28/87	<0.4	0.99	<0.03	22.2	0.60	515	760
Mean						16.4	0.83	496	770
3	W	08/27/87	<0.4	<0.30	<0.03	40.0	0.23	422	460
3	W	08/28/87	<0.4	<0.30	<0.03	47.8	0.28	445	530
3	W	08/28/87	<0.4	<0.30	<0.03	44.9	1.55	542	950
3	W	08/28/87	<0.4	<0.30	0.37	41.5	0.39	555	1150
3	W	08/28/87	<0.4	0.49	0.35	48.1	0.38	515	760
Mean						44.5	0.57	496	770
4	VM	09/03/87	<0.4	<0.30	0.32	18.5	0.67	545	762
4	VM	09/03/87	0.43	<0.30	<0.03	20.8	1.33	512	760
4	VM	09/03/87	<0.4	1.24	0.62	46.9	1.62	532	729
4	VM	09/03/87	<0.4	0.69	<0.03	22.2	0.40	499	714
4	VM	09/03/87	<0.4	<0.30	<0.03	34.5	0.59	442	468
Mean						28.6	0.92	506	687

Table 9, Cont.

Site	Tissue	Date	As	Be	Cd	Fe	Hg	TL	WT
4	DM	09/03/87	<0.4	<0.30	<0.30	18.1	0.93	545	762
4	DM	09/03/87	0.73	<0.30	<0.30	20.2	1.25	512	760
4	DM	09/03/87	<0.4	<0.30	0.45	20.5	1.38	532	729
4	DM	09/03/87	<0.4	<0.30	<0.30	27.0	0.98	499	714
4	DM	09/03/87	<0.4	<0.30	<0.30	26.1	0.60	442	468
Mean						22.4	1.03	506	687
4	W	09/03/87	<0.4	<0.30	<0.03	60.5	0.75	545	762
4	W	09/03/87	<0.4	0.40	<0.03	46.0	0.82	512	760
4	W	09/03/87	<0.4	<0.30	<0.03	90.7	0.81	532	729
4	W	09/03/87	<0.4	<0.30	<0.03	40.2	0.88	499	714
4	W	09/03/87	0.41	<0.30	<0.03	35.0	0.50	442	468
Mean						54.5	0.75	506	687

[a] DM = Dorsal Muscle, VM = Ventral Muscle, W = Whole Body; [b] Total length; [c] Weight; [d] Where concentrations of two or more replicates were < LOD, means were not calculated. LODs (mg/kg dry weight) were as follows: As 0.4, Be 0.30, Cd 0.03, Fe 5.0, Hg 0.02.

Table 10. Tissue metal concentrations (mg/kg dry weight), total length (mm), and weight (gm) in Arctic grayling (*Thymallus arcticus*) tissue from Selawik National Wildlife Refuge, Alaska, 1987

.

Site	Tissue[a]	Date	Cd	Fe	Hg	TL[b]	WT[c]
2	VM	08/27/87	<0.03	29.5	0.21	648	499
2	VM	08/27/87	<0.03	25.8	0.19	340	366
2	VM	08/27/87	<0.03	41.9	0.25	387	429
2	VM	08/27/87	0.64	28.7	0.29	383	463
2	VM	08/27/87	<0.03	36.5	0.36	369	402
Mean[d]				32.5	0.26	425	432
2	DM	08/27/87	<0.03	24.1	0.30	648	499
2	DM	08/27/87	0.58	17.7	0.15	340	366
2	DM	08/27/87	<0.03	23.3	0.27	387	429
2	DM	08/27/87	<0.03	20.5	0.27	383	463
2	DM	08/27/87	<0.03	29.8	0.42	369	402
Mean				23.1	0.28	425	432
2	W	08/27/87	<0.03	53.6	0.17	648	499
2	W	08/27/87	<0.03	73.2	0.11	340	366
2	W	08/27/87	0.34	107.0	0.16	387	429
2	W	08/27/87	0.62	44.0	0.12	383	463
2	W	08/27/87	0.35	102.0	0.16	369	402
Mean				75.9	0.14	425	432

[a] DM = Dorsal Muscle, VM = Ventral Muscle, W = Whole Body;
[b] Total length; [c] Weight;
[d] Where concentrations of two or more replicates were < LOD, means were not calculated. LODs (mg/kg dry weight) were as follows: Cd 0.03, Fe 5.0, Hg 0.02.

1988. Five northern pike were collected at Site 4 (Kobuk River below Squirrel River) and five Arctic grayling were collected from Site 7 (Lower Klery Creek) in 1988. Kidney, liver, and muscle samples were collected from each fish; however, for most samples, insufficient sample was collected to allow analysis for metals other than mercury. QA/QC screening indicates that beryllium, cadmium, nickel, thallium, and mercury data are acceptable from 1988 tissue samples (Table 11). Beryllium and thallium were not detected in any sample, cadmium was detected in 1 of 15 samples (1.0 mg/kg in a kidney sample at Site 4), nickel in 5 of 15 samples, and mercury in 24 of 25 samples. Nickel was detected in

3 of 10 northern pike and 2 of 5 Arctic grayling sampled. Nickel concentrations ranged from <2.0 mg/kg to 25.7 mg/kg (Table 11). Mercury concentrations in tissues ranged from <0.1 mg/kg to 3.90 mg/kg. During 1988, neither northern pike nor Arctic grayling kidney, liver or muscle tissue metals concentrations were significantly correlated with any water quality parameter.

In comparisons using data from both years, the two highest mean mercury concentrations in fish muscle tissue were at Site 4 (northern pike) for 1987 and 1988. Analysis of length, weight, and mercury concentrations in northern pike muscle, using stepwise multiple regression, revealed that mercury concentrations did not significantly add to the explanation of weight by length.

Table 11. Metals concentrations of kidney, liver, and muscle (mg/kg dry weight), and total length (mm) and weight (gm) of Arctic grayling (*Thymallus arcticus*) and northern pike (*Esox lucius*) collected from Selawik National Wildlife Refuge, Alaska, 1988.

Site	Species[a]	Tissue[b]	Date	Ni	Hg	TL[c]	WT[d]
4	NP	K	07/11/88	3.8	3.40	619	1375
4	NP	K	07/11/88		0.75	561	1120
4	NP	K	07/11/88	<2.0	0.28	510	880
4	NP	K	07/11/88		0.90	485	720
4	NP	K	07/11/88	<2.0	0.12	535	920
Mean[e]					1.09	542	1003
4	NP	L	07/11/88	<2.0	0.75	619	1375
4	NP	L	07/11/88	<2.0	<0.10	561	1120
4	NP	L	07/11/88		2.00	510	880
4	NP	L	07/11/88		0.33	485	720
4	NP	L	07/11/88		0.58	535	920
Mean					0.92	542	1003
4	NP	M	07/11/88	<2.0	3.90	619	1375
4	NP	M	07/11/88	<2.0	2.20	561	1120
4	NP	M	07/11/88	2.1	1.60	510	880
4	NP	M	07/11/88	25.7	1.50	485	720
4	NP	M	07/11/88	<2.0	1.50	535	920
Mean					2.14	542	1003
7	AG	K	07/10/88		0.55	405	605
7	AG	K	07/10/88		1.40	396	505
7	AG	K	07/10/88			359	410
7	AG	K	07/10/88			342	395
7	AG	K	07/10/88			328	365
Mean					0.97	366	456
7	AG	L	07/10/88		0.29	405	605
7	AG	L	07/10/88		0.41	396	505
7	AG	L	07/10/88		1.90	359	410
7	AG	L	07/10/88			342	395
7	AG	L	07/10/88			328	365
Mean					0.87	366	456
7	AG	M	07/10/88	3.6	0.42	405	605
7	AG	M	07/10/88	12.5	1.00	396	505
7	AG	M	07/10/88	<2.0	2.20	359	410
7	AG	M	07/10/88	<2.0	0.33	342	395
7	AG	M	07/10/88	<2.0	0.24	328	365
Mean					0.84	366	456

[a] NP = Northern Pike, AG = Arctic Grayling; [b] K = Kidney, L = Liver, M = Muscle; [c] Total Length; [d] Weight; [e] Where concentrations of two or more replicates were < LOD, means were not calculated. LODs (mg/kg dry weight) were as follows: Ni 2.0, Hg 0.1.

DISCUSSION

In 1987, active mining occurred upstream of two sampled sites: Sites 4 and 6 on the Kobuk River, below and above the Squirrel River, respectively. Mining occurred during 1987 upstream of Site 4, on both Klery and Timber creeks in the Squirrel River drainage, and upstream of Site 6, on Westly Creek in the Kobuk River drainage. During 1988, the only active mining was upstream of Site 4, at the Timber Creek mine (S. Lundeen, Bureau of Land Management, pers. comm.; J. Fogg, Alaska Department of Natural Resources, pers. comm.). The Timber Creek and Klery Creek mines are approximately 113 km (70 miles) and 89 km (55 miles), respectively, upstream of Site 4. The Westly Creek mine is approximately 225 km (140 miles) upstream of Site 4. Although the distances between these active mines and Sites 4 and 6 are great, they do not preclude mining effects on streams at the referenced sample sites. Weber Scannell (1992) found a 75% reduction in benthic invertebrate densities 92 km (57 miles) below mining activity in a heavily mined area. Sediments from mining activities could be seen as far as 160 km (100 miles) downstream from the source in some drainages (Weber and Post 1985).

Water Quality

Water quality characteristics of streams sampled during this study are typical of pristine calcium-magnesium bicarbonate systems. These characteristics include neutral to slightly basic pH, low conductivity, low to moderate hardness, and low to moderate alkalinity. The surficial geologies of Klery Creek (Sites 7 and 8) and the Squirrel River are primarily marble and limestone, respectively (Karl et al. 1989), and this is reflected in the water quality data. Conductivity, pH, alkalinity, and hardness at Sites 1 (Kugarak River) and 2 (Selawik River) were significantly less than at any other site. Similarly, pH values at Site 3 (Tagagawik River) are significantly lower than at any site other than Sites 1 and 2. Conductivity, alkalinity, and hardness at Site 3 were also less than at Sites 4 (Kobuk River below the Squirrel River), 6 (Kobuk River above the Squirrel River), 7, and 8, although not statistically different. Even though portions of the drainages at Sites 1, 2, and 3 contain mineralized areas, water quality at these sites appears to be determined by wetland/lacustrine inputs in the vicinity of the sample sites. Generally, the values for conductivity, alkalinity, and hardness are very similar to those reported by Snyder-Conn et al. (1992a) for the Koyukuk and northern Innoko National Wildlife Refuges, to the southeast of the Selawik Refuge, but hardness and alkalinity are lower than in the Nowitna National Wildlife Refuge (Snyder-Conn et al. 1992b). Values of pH from this study are generally higher than those in the Koyukuk Refuge (Snyder-Conn et al. 1992a). Values of pH at Sites 4, 6, 7, and 8 from this study are generally higher than at the Nowitna Refuge (Snyder-Conn et al. 1992b).

Values of pH at Sites 1, 2, and 3 are a pH unit less than those at other sites reflecting the acid conditions of peat marshes and lakes. This, combined with the low hardness and alkalinities at these sites, may increase the mobility of metals and contamination in aquatic organisms. Competition for binding sites on gill membranes between calcium and other divalent or trivalent metallic ions influences their uptake and toxicity in fish (Hunn 1985). Low alkalinities at these sites indicate poor buffering potential. Such areas are more susceptible to pH changes due to acidification events such as acid rain, snowmelt, the introduction of organic acids from peats, and acid mine runoff. Decreased pH can result in an increased release of metals into the water (Salomons and Forstner 1984), thus increasing their bioavailability (Haines et al. 1987).

Turbidities were low for all sites except Site 8 (upper Klery Creek, 49.9 NTU); the cause of the turbidity at Site 8 is unknown. Otherwise, turbidities from this study are lower than those measured in rivers on the Koyukuk and Nowitna Refuges (Snyder-Conn et al. 1992a, b).

Several statistically significant differences occurred that are not likely to be ecologically significant. These differences are due to very low variation within some sample sets. For

example, during both years turbidity values showed several statistically significant differences; however, the only likely ecologically significant difference is between Sites 1 through 7 (0.1 to 4.2 NTU) and Site 8 (49.9 NTU). Data from 1988 had significant differences among pH values at Sites 4, 6, 7, and 8. These differences were small and within the range of natural variation.

Only Site 4 (Kobuk River below Squirrel River) was sampled during both 1987 and 1988. Although a significant difference in water quality parameters occurred between these years, the variation is within normal interannual ranges for these parameters. Seasonal variations may also have affected the results because samples at this site were collected during September in 1987 and during July in 1988.

Trace Elements

Water

Several mean metal concentrations exceeded the WQC (EPA 1986). During 1987, total cadmium was present in concentrations exceeding both the chronic and acute WQC (EPA 1986) at Sites 1 (0.004 mg/L) and 2 (0.006 mg/L), and the chronic WQC at Site 3 (0.002 mg/L). Mean total recoverable cadmium concentrations at Site 1 (0.004 mg/L) also exceeded both the chronic and acute WQC (EPA 1986). Mean dissolved cadmium concentrations at Site 3 (0.002 mg/L) exceeded the chronic WQC (EPA 1986). Snyder-Conn et al. (1992a) found only trace amounts (0.0005 mg/L) of cadmium in water during 1988 in the Koyukuk Refuge. At the Nowitna Refuge, Snyder-Conn et al. (1992b) found cadmium up to 0.002 mg/L at one site during 1987, and only trace amounts (0.0005 mg/L) at one of five sites during 1988.

Cadmium can damage both plant and animal cells and is extremely toxic to chloroplasts and mitochondria (Stewart-Pinkham 1991). Cadmium is toxic to freshwater fish at varying concentrations depending on the developmental stage of the fish. For example, the LC50 of cadmium in rainbow trout (*Oncorhynchus mykiss*) is 0.001 mg/L for parr and 0.0029 mg/L for smolt (Moore and Ramamoorthy 1984). These concentrations are within the range found at Sites 1, 2, and 3 of this study. However, the toxicity and availability of cadmium varies widely depending on environmental conditions. Definitive relationships between cadmium concentrations and toxic effects are difficult to establish (Sorensen 1991).

Dissolved copper concentrations exceeded both the chronic and acute WQC (EPA 1986) at Sites 1 (0.020 mg/L), 2 (0.029 mg/L), 3 (0.020 mg/L), and 4 (0.017 mg/L). Total and total recoverable copper analyses did not pass the QA screen. Most unpolluted waters range from 0.0005 - 0.001 mg/L dissolved copper (Moore and Ramamoorthy 1984). Copper has been shown to have sublethal effects to salmon fingerlings in concentrations as low as 0.02 mg/L (Grande 1967). Hamilton and Buhl (1990) reported a 96-hr LC50 for chinook salmon fry (*Oncorhynchus tshawytsha*) of 0.054 mg/L. Acute toxicities have been documented for juvenile Arctic grayling within the range of copper concentrations found in this study (Buhl and Hamilton 1990). A lowest observed effect concentration of copper for avoidance behavior by rainbow trout has been reported as low as 0.0001 mg/L (Folmer 1976 cited by Atchinson et al. 1987).

Water hardness levels significantly influence toxic effects of metals due to the competitive inhibition of cations (Moore and Ramamoorthy 1984; Rand and Petrocelli 1985). Waters with low hardnesses, as found in this study, result in lower LC50s due to metals toxicity than do harder waters. Waters with lower pH levels, such as at Sites 1, 2, and 3 in this study, also accentuate the toxic effects of metals. For example, Nelson et al. (1986) reported that increases in pH from 6.6 to 8.7 increased the total and dissolved copper LC50s in fathead minnow (*Pimephales promelas*) larvae. However, one factor mitigating toxicity due to metals is the

complexation of metals by organic compounds such as humic acids. Humic materials in freshwaters bind more than 90% of total copper (Moore and Ramamoorthy 1984) and could be a factor at sites 1, 2, and 3 which drain boggy wetlands. Thus, elevated copper concentrations at Sites 1, 2, and 3 may not adversely affect local fish populations. Cadmium forms moderately stable complexes with a variety of organic compounds in typical lake water. However, in one study, humic acid complexation of cadmium accounted for only 2.7% of total cadmium (Moore and Ramamoorthy 1984). In any case, the concentrations of copper, chromium, and cadmium, in this study, were less than 10 times the LOD and should be considered semi-quantitative, and not cause for concern until better quantitation methods are used to verify these data.

With several exceptions, the analytical results of samples collected above (Site 6) and below (Site 4) the confluence of the Squirrel and Kobuk rivers were similar. Site 6 had higher manganese and much higher iron concentrations than Site 4. Sample Site 4 is several miles downstream of the confluence of the Kobuk and Squirrel rivers so complete mixing should have occurred before this point, suggesting that the Squirrel River had a profound influence on the Kobuk River for these two parameters. Neither iron nor manganese were detected in samples collected at Klery Creek, Sites 7 and 8, upstream of Site 4; therefore, mining activity at this site is likely not the source of these metals.

During 1988, total mean iron concentrations at Site 6 (1.660 mg/L) and mean lead concentrations at Site 7 (0.028 mg/L) exceeded the chronic WQC (EPA 1986). Again, these concentrations were less than 10 times the LOD and should, therefore, be considered semi-quantitative. High iron concentrations are not unusual in Alaska. Snyder-Conn et al. (1992b) reported total iron concentrations of up to 5.1 mg/L and 3.25 mg/L for 1985 and 1987 data, respectively, at the Nowitna Refuge. In addition, Snyder-Conn et al. (1992a) reported total iron concentrations up to 7.29 mg/L in the Koyukuk Refuge.

Although copper and chromium concentrations at Site 4 exceeded the WQC (EPA 1986) during 1987, neither metal concentration was elevated during 1988. The samples collected above (Site 8) and below (Site 7) the placer mine on Klery Creek were identical in metals content except that lead was detected in two of three total recoverable samples at site 7 (the total metals analyses did not pass QA screening). This may be due to disturbance caused by the mine; however, a definitive conclusion cannot be made based on this small sample set.

Sediment

Sediment concentrations of 1987 (Sites 1, 2, 3, and 4) data for arsenic, beryllium, cadmium, copper, mercury, molybdenum, and zinc from this study are characteristic of uncontaminated sediments (EPA 1977; Moore and Ramamoorthy 1984; Eisler 1989; Beyer 1990; Bennet and Cubbage 1991). Mean barium values from this study were up to 465 mg/kg which, in some areas, would be considered very elevated (EPA 1977). Karl et al. (1985) performed semi-quantitative analyses of headwater sediments in an area of high mineralization in the Squirrel River drainage (Omar River), and reported concentrations of barium ($\bar{x}$ = 1,100 mg/kg), copper ($\bar{x}$ = 54 mg/kg), and zinc ($\bar{x}$ = 333 mg/kg). They considered these values to be greater than twice normal background concentrations. Even so, these values are far more than twice the maximum values of these metals found in this study (barium up to 491.0 mg/kg, copper up to 13.70 mg/kg, and zinc up to 58.3 mg/kg). Therefore, values for barium in this study are considered background. Selenium and silver were not detected in any sample. However, the limits of detection, 14.0 and 4.8 mg/L, respectively, were too high to detect even what would be considered high levels of these elements. Sediment concentrations of arsenic, beryllium, and copper during 1987 were less than those at the Koyukuk and Nowitna Refuges (Snyder-Conn et al. 1992a, 1992b). Mercury and zinc concentrations were less than those at the Nowitna Refuge (Snyder-Conn 1992b). Vanadium concentrations were similar to those of the 1988 data at the

Nowitna Refuge but much less than the 1987 Nowitna data although analytical error may be responsible for the between-year differences in vanadium concentrations (Snyder-Conn 1992b). Snyder-Conn et al. (1992b) reported a significant correlation between vanadium and zinc, which was also found in this study.

Aluminum, arsenic, and mercury concentrations did not significantly differ among sites, but barium, copper, vanadium, and zinc differed between at least two sites. However, no clear trend is apparent from these data. Arsenic binds to particulate matter and arsenic concentrations have been shown to be positively correlated with decreasing particle size in sediments (Moore and Ramamoorthy 1984). In this study, arsenic concentrations were positively correlated with turbidity.

The highest mercury concentration detected during 1987 was 0.04 mg/kg and no mercury was detected during 1988 at the LOD of 0.1 mg/kg. These data indicate that mercury was probably not present at anomalously high levels.

Fish Tissue

Cadmium was detected in 12 of 30 fish, and at each site sampled except Site 7 (fish tissue samples were not collected at Sites 6 and 8). Cadmium concentrations in fish tissue ranged from <0.5 to 1.0 mg/kg, the latter from a northern pike kidney. Cadmium is accumulated primarily in major organ tissues, particularly in gill, liver and kidney tissue (Eisler 1985), rather than muscle (Moore and Ramamoorthy 1984). These levels are less than those reported in Arctic char (*Salvelinus alpinus*) muscle (up to 2.3 mg/kg) from an unpolluted high Arctic lake (Bohn and Fallis 1978). In this study, in northern pike where cadmium was detected, cadmium concentrations are slightly greater than those of northern pike from the Koyukuk Refuge (Snyder-Conn et al. 1992a), where cadmium was detected in 6 of 8 fish, but similar to those where cadmium was detected in the Nowitna Refuge (Snyder-Conn et al. 1992b), where cadmium was detected in 10 of 21 fish. In general, cadmium residues in fish muscle cannot be related to concentrations in water (Moore and Ramamoorthy 1984), and no such correlations were found in this study.

The presence of mercury in fish tissue is widespread throughout the United States. EPA (1992) found mercury in fish tissue at 92% of 374 sites sampled in the contiguous 48 states. Mercury levels of approximately ≤2 mg/kg dry weight (assuming 75% moisture) were found at 85% of their sample sites. The mean mercury concentration of background sites was approximately 0.36 mg/kg dry weight (assuming 75% moisture). A study of whole fish from 109 sample sites nationwide, yielded a geometric mean mercury concentration of 0.4 mg/kg dry weight (assuming 75% moisture), 85% of which had ≤0.68 mg/kg dry weight mercury (assuming 75% moisture) (Schmitt et al. 1990). In this study, mercury was detected in each fish sampled regardless of location. Six of 15 northern pike and none of the 5 Arctic grayling collected in 1987 had whole body mercury concentrations >0.4 mg/kg. During 1988, all five northern pike collected and three of five Arctic grayling had mercury concentrations in muscle >0.4 mg/kg. One northern pike at Site 4 had moderately high mercury concentrations in muscle (3.90 mg/kg) and kidney (3.40 mg/kg), but not liver (0.75 mg/kg). The EPA (1992) and Schmitt et al. (1990) data are based on collections of many fish species with many different feeding habits. Northern pike are piscivores (Morrow 1980) and should be expected to bioconcentrate mercury at a higher rate than fish with other feeding habits (Forstner and Wittmann 1983; Wren and MacCrimmon 1983).

Mean mercury concentrations in fish muscle tissue at Site 4 were higher than at any other site for both years. Although elevated mercury tissue concentrations can be due to natural environmental concentrations of mercury (Moore and Ramamoorthy 1984), mercury concentrations in tissue at Site 4 are not explained by the sediment data. Mercury was detected

in sediment at Sites 1 and 3, but not Sites 4 or 7. Grayling (Sites 2 and 7) and northern pike (Sites 1, 3, and 4) are highly migratory species and, even under the most ideal conditions, it is difficult to attribute tissue contaminant burdens in these species to conditions at specific locations.

Nickel was detected in 3 of 10 northern pike in concentrations up to 25.7 mg/kg at Site 4, and in 2 of 5 Arctic grayling in concentrations up to 12.5 mg/kg at Site 7. These are comparatively elevated levels (Jenkins 1980; Moore and Ramamoorthy 1984). Nickel residues from industrialized areas seldom exceed 4 mg/kg dry weight (assuming 75% moisture) in fish tissue (Moore and Ramamoorthy 1984). Wren and MacCrimmon (1983) found up to 8.4 mg/kg dry weight (assuming 75% moisture) nickel in northern pike muscle from a Canadian Precambrian shield lake. The highest nickel concentration recorded in a survey of Pennsylvania fish from 14 sites was 0.41 mg/kg (Rompala et al. 1984). Nickel has been reported in concentrations up to 17.70 mg/kg in northern pike muscle from the Koyukuk Refuge (Snyder-Conn et al. 1992a), indicating that high nickel concentrations may be widespread in this area of Alaska. Nickel concentrations up to 1.09 mg/kg in Arctic grayling muscle and up to 2.72 mg/kg in northern pike muscle from the Nowitna Refuge were also reported (Snyder-Conn et al. 1992b). The source of the nickel is unknown. Nickel was not detected in water samples at Sites 6 and 7, and was detected in only one of three samples at Site 4, downstream of Site 6. Little information is available on the effects of nickel body burdens on fish and wildlife.

Iron was detected in every sample collected in 1987. Mean values of whole body analyses ranged from 27.04 mg/kg in northern pike at Site 1 to 75.96 in Arctic grayling at Site 2. Iron concentrations were highly variable, even within a tissue type, as was also observed by Snyder-Conn et al. (1992a, 1992b) in fish from other northern Alaskan rivers.

Differences among fish tissues. Dorsal muscle, ventral muscle, and whole body (minus the dorsal and ventral muscle samples) samples from 5 Arctic grayling and 15 northern pike collected during 1987 were analyzed separately. No significant differences occurred between dorsal muscle, ventral muscle, and whole body concentrations of mercury for these species. This appears to indicate that analytical results from these tissues may be compared with no loss of consistency between samples for mercury. This information may be useful when examining existing data. However, it is recommended that when muscle tissue is collected, all tissue should be collected from the same area of the body to facilitate better comparisons. Iron concentrations of grayling whole body samples were significantly greater than in all other tissues except northern pike whole body.

Differences between Arctic grayling and northern pike. Iron concentrations were not significantly different in northern pike versus Arctic grayling. Cadmium was detected occasionally in both species. Arsenic and beryllium were detected sporadically in northern pike and not at all in Arctic grayling. Mercury concentrations in muscle were significantly higher in northern pike than in Arctic grayling. Many factors affect inter- and intraspecific variation in accumulation and retention of mercury in fish including phylogenetic differences in metabolism, the presence of other metals (e.g., selenium), pH, alkalinity, mucous binding of mercury, age, and temperature (Sorensen 1991). Arctic grayling, although somewhat piscivorous, are primarily insectivorous (Armstrong 1986) and, consequently, mercury bioconcentration would not be expected to be as great in this species. Size appears to be excluded as a determining factor. No significant correlation existed, in either species, between length and weight, and metals concentrations in muscle. Similar findings regarding mercury concentrations in muscle were reported by Snyder-Conn et al. (1992b) from other northern Alaska river systems. However, positive correlations between age, length and mercury concentrations have been observed in other studies (Akielaszek and Haines 1981; Barak and Mason 1990). Migratory species, such as

northern pike and Arctic grayling, are subjected to varying exposures of contaminants. As a result, consistent relationships between growth and contaminant uptake are difficult to measure.

CONCLUSIONS

No effects of off-refuge placer mining were found on the Selawik Refuge during this study. Water quality characteristics of rivers sampled during this study are typical of pristine calcium-magnesium bicarbonate systems. Water quality parameters from the Kugarak (Site 1), Selawik (Site 2), and Tagagawik (Site 3) rivers appear to be influenced by the wetland/lacustrine region in the vicinity of the sample sites. Cadmium and copper concentrations at these sites were slightly elevated in water samples. This may be a result of increased mobilization of these metals due to the lower pH and hardness at these sites.

Sediment concentrations of arsenic, beryllium, cadmium, copper, mercury, molybdenum, and zinc at Sites 1, 2, 3, and 4 are characteristic of uncontaminated sediments. Although sediment barium concentrations are comparatively high, they are considered background for this area of Alaska.

Consistent with findings elsewhere in Alaska, mercury concentrations in fish tissue from this study were somewhat elevated. However, mercury concentrations remained below the U.S. Food and Drug Administration action level. Two of five nickel concentrations in northern pike muscle tissue on the Selawik Refuge (2.1 and 25.7 mg/kg) were elevated compared to those of other areas. Further study of nickel burdens in fish on the Selawik Refuge is warranted prior to drawing final conclusions based on these limited data.

Based on the results of samples from 15 northern pike and 5 Arctic grayling, mercury concentrations in dorsal and ventral muscle, and whole body analyses of these species may be used interchangeably, within each species, for tissue comparisons. However, we recommend comparisons based on tissues dissected from the same location on each fish sampled. Mercury concentrations in northern pike muscle were significantly higher than in Arctic grayling but within expected concentration ranges.

RECOMMENDATIONS

Nickel concentrations in three northern pike from the 1988 data set are quite high. Any further contaminants investigations conducted on the Selawik Refuge should include nickel analyses in liver and kidney tissue in both Arctic grayling and northern pike and should be directed towards establishment of a firm baseline for this contaminant.

The upper Kobuk River contains many areas with mineral occurrences and mining potential. Baseline data for water, sediment, and tissue should be collected from a site where the Kobuk River enters the Refuge. A comprehensive set of baseline data will aid the Service in determining impacts, if any, of mining in these areas. Another priority is to sample in the upper Kobuk River basin to establish upper Kobuk River baseline data for water quality and metals. If new mines begin operations, sampling should be done both above and below the mines to determine their impact.

Concentrations of several metals, (i.e., copper, chromium, cadmium, and lead) exceeded the WQC. Unfortunately, these data were generated using high LODs, resulting in poor quantitative reliability. Lower LODs should be adopted in future analytical studies. Further sampling should be conducted to establish a comprehensive set of baseline data for these toxic metals. Sites 1, 2, and 3, as well as others, should be included in this sampling. Other metals for which QA was inadequate should also be resampled to establish baseline data. These metals include aluminum, arsenic, beryllium, boron, cadmium, chromium, copper, lead, magnesium, manganese, mercury, molybdenum, selenium, strontium, thallium, tin, and zinc.

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APPENDIX A: DOCUMENTATION AND SAMPLE HANDLING

Study Proposals

A study proposal was submitted prior to each year of sampling. Both the 1987 and 1988 study plans were prepared by Selawik 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 study including a review of related research, a methods section including discussion of collection and analysis procedures, topographic maps indicating anticipated sample locations, and a cost proposal based on the number and types of samples to be collected.

Field Documentation

During field studies, sample documentation was recorded in a weatherproof field notebook in permanent ink. The date and time of collections at each site were specified as were the water temperature at the sample site and results of all water quality analyses. Sample identifications were also listed by sample type for each sample collected. Data on fish species, including whole weight, tissue weights (if applicable), fork length, and total length were also recorded 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 sample preservation and storage; instructions to the laboratory, including a description of the analyses requested together with the suggested analytical method; a list of data recipients; a cost estimate for the requested analyses; and a tabulated summary of information on each sample. This information included the sample identification, the date of collection, the type of sample or tissue, the species (for fish), the sample location, sample weight or volume, and analyses requested for each particular sample. The catalogs were submitted to the following analytical laboratories:

Catalog	Regional I.D.	Laboratory Address
5445	R78733F	Research Triangle Institute Cornwallis Rd. P.O. Box 12194 Research Triangle Park, NC 27709
5742	R788121	Versar, Inc. 6850 Versar Center Springfield, VA 22151

Catalogs were inspected by a Quality Assurance Officer at the Patuxent Analytical Control Facility. Upon approval, they were forwarded to the laboratory together with the listed samples. Laboratory data were received by the authors following review and approval by the Quality Assurance Officer.

Chain of Custody

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

Sample Preservation/Storage and Shipment

Samples for total metals and total recoverable metals analysis were acidified with 2-mL HNO_3 (Ultrix). Samples for dissolved metals analysis were acidified with either 1-mL (1987) or 1.2-mL (1988) HNO_3 (Ultrix). Water, sediment, and fish samples were placed in coolers with ice, or blue ice, and transported by boat, float plane or helicopter to Kotzebue, Alaska, for temporary storage. Water samples were refrigerated from the date of collection until shipment; sediment and fish tissues were kept frozen. Samples were shipped to the laboratory by air courier. Water samples were shipped with ice; frozen samples were shipped with dry ice.

Sample Holding Times

Holding times for Catalogs 5445 and 5742 were 13 and 15 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, losses may have also occurred. However, it is uncertain whether losses due to excessive holding times are significant.

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 Database 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	88SE501ARK	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	SE	Selawik NWR	See codes
SI	Sample site number	01	Sites are assigned permanent numbers by refuge or location	Sequential
N	Sample session[1]/ overflow[2]	Numeric or alphabetic	Sample period for multiple samples/yr or overflow use	Sequential letters or numbers
R	Replicate designator	A	Alphabetic indicating Replicate A at Site 01	Sequential letters
S	Species code or type of sample	F	Fish	See codes
T	Type/tissue	L	Liver	See codes

Auxiliary Fields

Field Name	Field Description	Example	Entry Description	Comment
SEX		M, F, U	Male, female or unknown	Samples of biota only
DATE	Sample date	12/13/90		
SPECIES	Genus and species	Esox lucius	northern pike	Samples of biota only

NO IN COMP	Number of Organisms in composite sample	18	If 18 sculpin were in a sample	Samples of biota only
SAMPLE WT	Weight of submitted sample in grams	43	43 gm = weight of liver	Weight of discrete organs or subsamples
TOTAL WT	Total weight of organism or sample if subsampled	100	100 gm = weight of whole fish	Weight of whole, original sample or organism
TLGTH	Organism's total length (mm)	25	25 mm = total length of fish	Samples of biota only
FLGTH	Fork length (mm)	23	23 mm = fork length of fish	Fish only
UNIT	Unit of analysis	ppm, 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[3]
Detection Limit (shown as X and the metal symbol)	Less than for each metal	<	Used when value measured is less than detection limit	
As (Example)	Metal concentration	5.5	5.5 mg/kg	See basis and unit

[1] Number (#) is that of sample period at a site that year (e.g., for first sample date at a site, N = 1, the next sample date at the site within the year N = 2, etc.).
[2] Overflow is to be used when necessary to form a unique ID when S & T fields are the same for the sample site and sample period or when there are more than 99 sample locations. When not used for this purpose, it can be used to designate whether metals (M) or hydrocarbons (H) are to be analyzed.
[3] Concentrations in water are always reported on a wet weight basis. However, labs vary in how other matrices are reported.

General Location Codes

AA - Arctic NWR	YF - Yukon Flats NWR	SE - Selawik NWR
BA - Barrow	CR - Chena River	NO - Nowitna 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)	CP - Cape Pierce
DP - Denali Park	TE - Tetlin NWR	SL - St. Lawrence Is.

Species Codes

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

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

If the study involves known species, use these codes:

Fish

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

Birds

A - osprey	F - phalarope	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
	K - boreal owl	

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
D - dissolved metals (H_2O)	F - feather	U - shoots
R - tot. recov. metals (H_2O)	A - sand (2.0 to .0625mm)	V - leaves
T - total metals (H_2O)	L - clay (<.0039mm)	
	Z - stem	
S - stomach	I - silt (.0625 to .0039mm)	

APPENDIX C: QUALITY ASSURANCE/QUALITY CONTROL 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, Laurel, Maryland, to determine the inorganic and organic composition of samples.

Contract laboratories are selected by a PACF technical committee using a process involving the correct analysis of samples submitted to prospective laboratories by PACF, and a careful review of the laboratory, its procedures, facilities, experience, and personnel. A final step in selecting a laboratory is an on-site inspection by representatives of the evaluation committee. Continued round-robin testing and cross-checking of contract laboratories by PACF have been used to monitor their performance and alert the Service's Quality Assurance Project Officer of systematic analytical problems with particular analytes. Approximately 5% of all sample catalogs submitted for analysis to contract laboratories are also reanalyzed by PACF. In addition to these QA/QC measures, precision, accuracy, and potential laboratory contamination of samples are evaluated through the analysis of specific quality control samples. Reports produced by contract laboratories are required to contain the following:

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

2. The analytical results.

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

    a. Limits of detection for each sample
    b. Duplicate analysis
    c. Spiked sample analysis
    d. Standard reference material (SRM) analysis
    e. Procedural blank analysis

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

The laboratory may also be required to submit copies of all raw data and control charts collected during the analysis upon request. In addition to a brief description of the methods, we have typically requested that the laboratory provide a description of detailed methods, and the specific instrumentation used, including model numbers.

PACF determined that the analytical laboratory used for the 1987 samples did not produce sufficient QA/QC data for them to estimate confidence intervals. Estimated 95% confidence intervals for 1988 sample analyses are listed in Table 1.

Table 1. Estimated 95% confidence intervals for all matrices of ICP and AA analyses, 1988.

Sample Concentration	ICP Analyses	AA Analyses
0 - 2 X LOD[a]	± 200%	± 200%
2 - 10 X LOD	± 40%	± 10%
> 10 X LOD	± 20%	N/A[b]

[a] Limit of Detection
[b] N/A = Not Available

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

Limits of Detection

The criterion "limit of detection" (LOD) has been variously defined and its determination is the subject of controversy (APHA et al. 1989). Depending on the laboratory performing the analyses, the LOD referenced could refer to the instrumental detection limit for a given sample, the typical "method" detection limit, the lower limit of detection for all samples, or the limit of quantitation, above which results can be viewed as semi-quantitative or quantitative. A general definition for LOD is that it is the lowest concentration level that can be distinguished statistically from a blank sample. That is, it is a reliable limit for an analyte, above which values are "real" and distinguishable from instrument noise. Samples reported as being below the detection limit in a data set are generally reported as <X where X is the 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. Because the method LOD actually varies depending on the nature of the individual sample, the upper LOD reported for each matrix in a sample catalog was adopted as the limit of detection for the QA/QC screening of the data.

Analytical Precision

Precision refers to the degree of agreement among repeated measurements of a given sample and is not a measure of accuracy. Precision varies with such factors as the homogeneity of the sample, sample volume, sample matrix, instrumental method, instrumental drift, chemical interferences, and the analyte concentration in the sample. Estimates of precision used for this study were made using duplicate analysis, where two subsamples of a homogenized sample are collected and analyzed by the contract laboratory. Precision is monitored by the contract laboratory using range ratio control charts for each analyte of each matrix (water, sediment, tissue). The measure selected for estimating precision by our QA/QC program is the relative percent difference (RPD):

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

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

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

Since the LOD may vary according to sample, the LOD used in the QA/QC screening program is the highest LOD identified for each sample matrix in the sample data set. Average RPD's for each analyte and each matrix are calculated separately. For concentrations of an analyte > 2(LOD) and < 10(LOD), results are expected to be semi-quantitative, and dependent on their relation to the LOD. In these samples, both precision and accuracy may be reduced. For measurements greater than 10(LOD), analyses can be expected to be highly quantitative, and rigorous criteria are applicable to determine whether average precision is sufficient to guarantee repeatability. Samples with concentrations 2-10(LOD) or > 10(LOD) receive no qualifying label in the screening program Quality Control Analysis printout (i.e., the field is left blank).

The QA/QC software program first computes RPD's for all duplicate analyses performed for a given analyte, averages the RPD's for that analyte, and then compares the average to a criterion of 20%. Analytes with RPDs > 20% are rejected and analytes with RPDs < 20% are accepted.

Analytical Accuracy

Spiked Samples

In addition to precision, measurements of correctness of the analyses are needed to guarantee the quality of semi-quantitative (2-10 LOD) and quantitative (>10 LOD) data, and to estimate chemical interferences that may occur. One method used by Service contract laboratories to estimate accuracy and gauge interference is that of spiked samples. This method consists of dividing a homogenized sample into two subsamples, analyzing one as the sample, spiking the other subsample with a known quantity of one or more analytes, and analyzing the resulting mixture. The

difference between the two subsamples, after accounting for any differences in sample weight, is the spike recovery. This value is usually reported as a percentage of the amount added. Recovery rates greater than 100% may indicate that the instrument was incorrectly calibrated, subject to upward drift, or that contamination of the sample may have occurred. Recoveries of less than 100% could occur due to loss of the analyte during the sample procedure (e.g., loss of mercury due to volatility), instrument drift downward, errors in the calibration procedure, or chemical interferences inherent in the matrix being analyzed.

Another important reason for imprecise metal recoveries is incomplete digestion of the sample material. Unless specified in the catalog instructions, metal digestions performed by contract laboratories are incomplete, resulting in the release of some, but not all, of the analyte. Such digestions give what are referred to as "total recoverable metals" or "acid-soluble metals." The metals released are those that would be readily available for release in an acidic environment. Theoretically, these are the metal concentrations of biological significance, in terms of availability for rapid biogeochemical cycling. Metals that remain bound in the matrix are more tightly bound, either by chemical complexing or by physical processes, and may not become biologically available under any natural circumstance. Occasionally, total digestion (using hydrofluoric acid rather than nitric/perchloric acid) is performed when spike recoveries are not satisfactory during the partial digestion. In the case of catalogs in this study, sediments and tissues were subject to complete digestion; both complete and incomplete digestions were performed on water samples as described earlier.

Usually, the amount of spiking solution added to a sample is sufficient to result in a concentration of that analyte of more than twice the original concentration in the sample and greater than 2(LOD). The computer program used for this study examines spike recoveries for all spiked samples, even if the spike was low.

The spike recovery criteria adopted for the computer program, 80-120% average recovery, are based on Service criteria presented by Moore (1990) and APHA et al. (1989). The program identifies all analytes for which the average spike recovery (average of all spikes for that analyte and matrix) fails this test. These criteria are as stringent or more stringent than the APHA et al. (1989) criteria for performance evaluation samples of water and wastewater.

Standard reference materials (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 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 to attain than accuracy in performing spike analysis.

Sources of SRM's for the Selawik 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 spectrophotometry, X-ray fluorescence, and inductively-coupled plasma spectrometry). The certified value for each analyte, or "true value," is typically the weighted mean of the different methods. A standard deviation is also calculated and used to provide a certified range. The method for creating this range varies somewhat depending on the source of the analyte. In some cases, a considerable amount of professional judgement is used to define this range.

Some analyte values may 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 SRMs, consensus values, together with standard deviations (SDs), have been presented for many of these analytes (Gladney et al. 1987). These are values collated from published research by a variety of investigators.

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

If the mean value of an analyte as measured by the laboratory is within the range of the certified value ± 3 SD, the SRM data are considered acceptable or "good." For certified values greater than 2(LOD), a printout is also given of analytes for which the measured values fall outside ± 3 SD; these data are listed as questionable. On the QA/QC Summary Sheet for each catalog (Appendix D), "Low SRM" and "High SRM" show this confidence interval. Where the SD is not known, it is defined as 10% of the certified value. Use of 10% as the estimated standard deviation is based on examination of the average relationship between the mean and standard deviation for several NIST SRM's for a suite of metals. Typically, the standard deviation is 5 - 10% of the true value. For certified values ≥ 2(LOD), a printout is also given of analytes for which the measured values fall outside this range, listing these data as questionable.

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 ± 15% of the certified value (Freitas et al. 1989). However, it evaluates the laboratory performance in terms of accuracy achieved by the agency producing the SRM. Thus, greater accuracy is required for analytes for which measurement accuracy is typically higher than for difficult-to-quantify analytes.

The more SRM's used on a given matrix, the higher the probability that the laboratory will fail to meet acceptance criteria defined above in all tests. The final screening criterion developed for SRM evaluation avoids penalizing laboratories for performing additional testing. When more than one comparison with a given SRM is performed, we compared the mean measured value to the true value (or consensus value) ± 3 SD. Occasionally this average measured SRM value is <2(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 ± 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.

No field blanks were collected during the Selawik study. 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 only) cannot be ruled out. In addition, the occurrence of many nondetects in analyses of all matrices is an indication that systematic contamination during handling did not occur. However, such contamination was identified for 1988 dissolved metal samples which were higher in lead than complementary total and total recoverable metals samples.

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 be used to evaluate whether the equipment cleaning procedures are adequate. For this blank, double-distilled and/or deionized water is processed in the apparatus after it has been cleaned according to standard operating procedures and then analyzed along with the samples being processed. Matrix blanks are sometimes also used for sediment and tissue samples, and when a reagent blank analysis indicates contamination. A reagent blank is distilled and deionized water that is passed through the analytical procedure with the other samples. Reagent blanks are subjected to the same digestion procedures as samples. If contaminants are detected at levels that may compromise the results of the analysis and are not systematic, the above breakdown is needed to identify sources of contamination.

The laboratory may run a single blank through the entire analytical process, including sample preparation and reagent treatment. If contaminants detected during the entire process are negligible, then separate sample preparation and reagent blanks are not necessary. Also, if blank contaminant levels are recurring (i.e., nonrandom), the blank values may be subtracted from the data set. Blank samples used in quality control for the Selawik sample catalogs are summarized in Appendix D.

The QA/QC computer program examines blank contamination in relation to concentrations of each analyte detected in the duplicate analyses (presumably selected at random from the sample set). The maximum blank concentration of an analyte is compared to the mean analyte for the duplicates. If the maximum blank concentration exceeds 15 percent of the mean value for all the duplicates and if this concentration is above the maximum LOD, the blank value as a percentage of the mean duplicate concentration is reported, resulting in rejection of the data.

APPENDIX D: QA/QC SCREENING RESULTS (RAW DATA)

These data have not been included in this .PDF format document to make this file smaller.

QA/QC screening results are available from:

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