

# Geologic Studies in Alaska by the U.S. Geological Survey, 1994

Thomas E. Moore *and* Julie A. Dumoulin, *Editors*

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**COVER PHOTO:** View to the northeast of carbonate rocks (light colored rocks, foreground to left skyline) of the Lisburne Group (Mississippian and Pennsylvanian) and of the Baird Group (Devonian) overlain on a moderately east-dipping fault contact by ultramafic rocks (dark rocks to right of light colored rocks) of the Avan Hills mafic-ultramafic complex (Jurassic), western Brooks Range. The emplacement mechanism of the Siniktaneyak mafic-ultramafic complex, which is also located in the western Brooks Range and is similar to the Avan Hills mafic-ultramafic complex, is the subject of a paper by Morin and Moore in this volume.

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# Environmental Geochemistry of Mercury Deposits in Southwestern Alaska: Mercury Contents in Fish, Stream-Sediment, and Stream-Water Samples

By John E. Gray, Allen L. Meier, Richard M. O'Leary, Carol Outwater, and Peter M. Theodorakos

## ABSTRACT

Mercury is a heavy metal that can be toxic to humans when concentrations are high, especially in food sources. Mercury-rich lodes and abandoned mines scattered throughout southwestern Alaska represent a potential environmental hazard in the region. Concentrations of mercury were measured in fish, stream-sediment, and stream-water samples collected downstream from the mines and lodes to evaluate environmental mercury accumulation. Mercury concentrations in fish are useful for addressing the levels of mercury in the food chain that can eventually affect humans.

Freshwater fish collected downstream from the mercury lodes generally contain the highest mercury concentrations. Dolly Varden collected downstream from the Cinnabar Creek mine contain as much as 0.62 ppm Hg wet weight in muscle samples (edible fillets), but mercury concentrations are also elevated in Arctic grayling collected downstream from the Mountain Top mine (as much as 0.26 ppm in muscle samples) and at a site on the Kolmakof River (as much as 0.42 ppm Hg in muscle samples). The site studied on the Kolmakof River is downstream from mercury anomalies that suggest a possible undiscovered mercury lode. Arctic grayling and Dolly Varden, collected from background sites in southwestern Alaska, contain as much as 0.20 ppm Hg wet weight in muscle samples. Chum salmon collected from large rivers in southwestern Alaska contain the lowest mercury concentrations in muscle samples collected in the study, ranging up to 0.08 ppm Hg wet weight. The salmon results are important because these fish are a major food source to residents, and the low mercury concentrations suggest that mercury from the mines and deposits has not adversely affected the salmon. All mercury concentrations in fish collected in this study are below the 1 ppm wet weight concentration for edible fish established by the Food and Drug Administration (FDA) as the action level when mercury advisories are listed and sale of fish is restricted. In addition, all concentrations of mer-

cury in stream-water samples collected in the study are below the 2-ppb drinking-water maximum-contaminant level recommended by the State of Alaska.

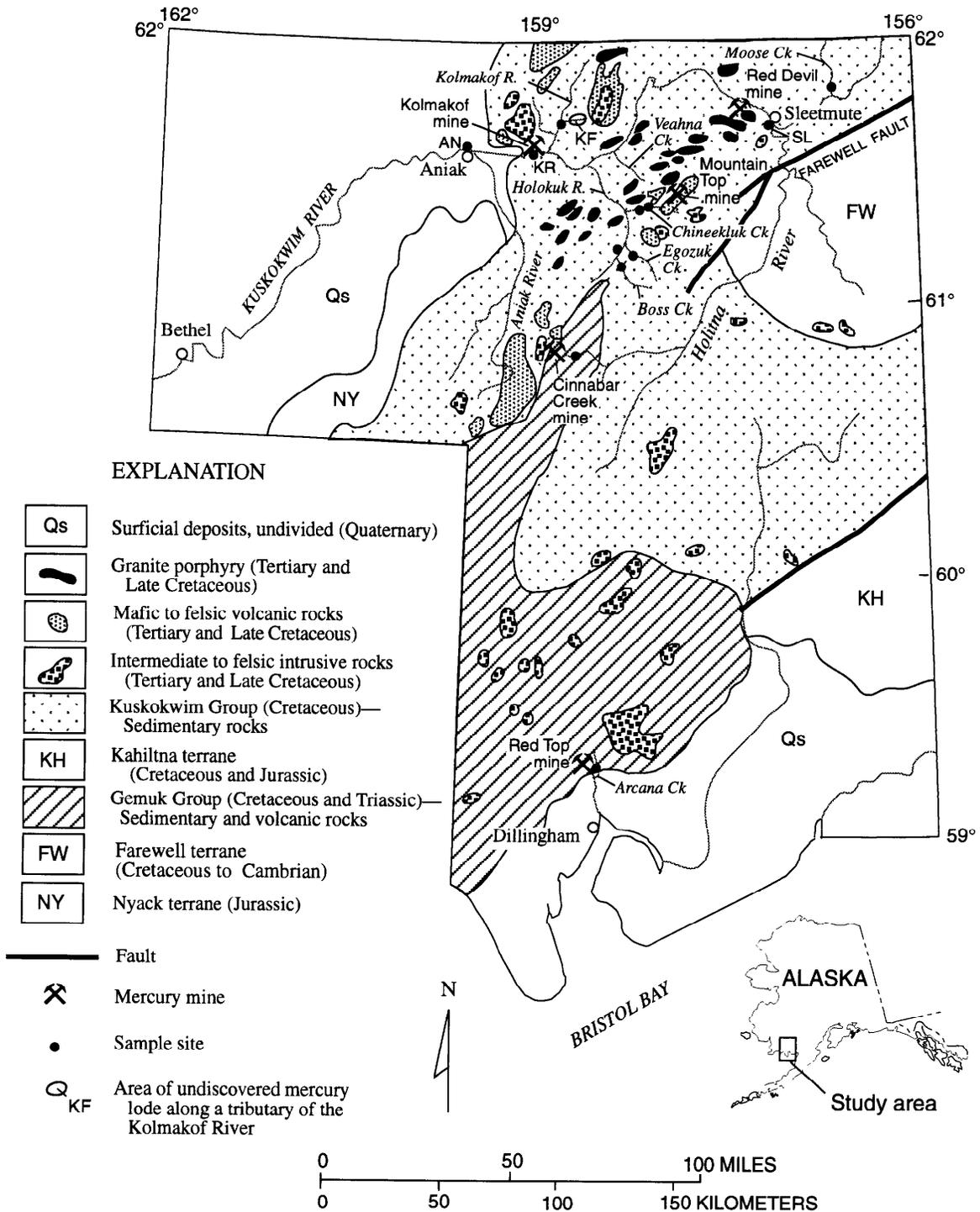
## INTRODUCTION

Mercury is a heavy metal of environmental concern because elevated concentrations can be toxic to living organisms. Mercury has no known metabolic purpose, and contaminations are regarded as undesirable and potentially hazardous (National Academy of Sciences, 1978). Present and past mercury uses include manufacture of electrical instruments, pharmaceuticals, plastics, agricultural fungicides, paper production, munitions, and in the extraction of gold (amalgamation) in mining. Most mercury toxicity problems are related to organic mercury compounds (Eisler, 1987), of which methylmercury is the most toxic to humans (Friberg and Vostal, 1972). Conversion of inorganic forms of mercury (for example, cinnabar) to methylmercury is mostly by the action of aerobic and anaerobic bacteria in organic-rich muds in streams and lakes (Wood, 1974; Gough and others, 1979). Methylmercury is volatile, water soluble, and concentrates in tissues (bioaccumulation) of fish and other aquatic organisms (Fenchel and Blackburn, 1979). Once mercury is converted to water-soluble forms, like methylmercury, it becomes readily available to biota (bioavailable), such as fish. Mercury can increase in concentration with increasing trophic position in the food chain (biomagnification). Concentration of mercury in fish provides an easy pathway for mercury to enter the food chain. The toxic nature of mercury has stimulated abundant environmental research (for example, Lindqvist, 1991).

Mercury lodes are scattered over a wide region covering several thousand square kilometers in southwestern Alaska (fig. 1). Several of the lodes were mined between the early 1900's and the 1980's, but they are not currently operating because of low prices and low demand for mercury. Approximately 41,000 flasks of mercury (1

flask=76 lb or 34.5 kg) have been produced from the region (Bundtzen and others, 1986). The presence of mercury lodes and abandoned mines in southwestern Alaska is

a potential hazard to residents and wildlife populations because drainage from the lodes and mines enters streams and rivers that are part of local ecosystems.



**Figure 1.** Location map of study area. Samples sites along the Kuskokwim River are AN (near Aniak), KR (near Kolmakof), and SL (near Sleetmute). Geology generalized from Cady and others (1955), Hoare and Coonrad (1959), Miller and others (1989), and Miller and Bundtzen (1994).

Environmental studies are an important part of the U.S. Geological Survey's (USGS) mineral resource assessment program. This study is part of continuing environmental investigations of mercury-rich mineral deposits in southwestern Alaska. Environmental studies of the southwestern Alaska mercury mines and deposits were recently initiated by the USGS (Gray and others, 1994); other studies conducted by the U.S. Fish and Wildlife Service provide baseline data for mercury in fish (Crayton, 1990; Snyder-Conn and others, 1992). Gray and others (1994) reported that fish (Arctic grayling), stream-sediment, and stream-water samples collected downstream from the Cinnabar Creek mine contained mercury concentrations elevated above those collected from a control site. However, Gray and others (1994) noted that the fish collected from Cinnabar Creek were unusually small, and any larger, predatory fish in Cinnabar Creek could potentially contain higher mercury concentrations. This is because mercury concentrations generally increase in larger predatory fish as a result of biomagnification (Eisler, 1987). Thus, fish higher in the food chain also need to be evaluated. Cinnabar Creek was the only southwest Alaska mercury deposit evaluated by Gray and others (1994), but widespread mercury lodes and mines in the region suggest that environmental aspects of other lodes must be evaluated in relation to well-constrained regional backgrounds (sites where no mercury lodes are known upstream). In addition, mercury concentrations in salmon and pike need to be evaluated because these fish are a common food source and the presence of mercury lodes throughout southwestern Alaska suggests that mercury might be elevated in these fish. Thus, the objectives of this study are to measure mercury concentrations in samples of fish, stream-sediment, and stream-water collected (1) downstream from several mines and lodes and (2) from several sites where no mercury lodes are known in order to thoroughly evaluate regional geochemical backgrounds. Mercury concentrations were also measured in salmon and pike to determine if these food sources contain elevated mercury. These data were then used to evaluate mercury hazards of the mercury mines and lodes in southwestern Alaska. Other heavy metals such as As, Cd, Pb, Cu, Sb, and Zn were also measured in the samples because these metals can also be of environmental concern. Sites were studied downstream from the Cinnabar Creek, Mountain Top, and Red Top mines, as well as a locality on the Kolmakof River downstream from a probable undiscovered mercury occurrence (fig. 1). These localities were chosen for study because streams draining the mines and lodes were large enough to support fish habitat. Samples were collected from background sites on Boss Creek, Egozuk Creek, Holokuk River, Moose Creek, and Veahna Creek (fig. 1). Salmon were collected from two sites along the Kuskokwim River (one at Aniak and one adjacent to the Kolmakof mine) and from the background site on the

Holokuk River. Northern pike were collected from a site on the Kuskokwim River near Sleetmute.

## GEOLOGY

Rocks in the study area primarily consist of sedimentary and volcanic rocks of the Triassic and Cretaceous Gemuk Group and the Cretaceous Kuskokwim Group. The Gemuk Group consists of massive siltstone interbedded with lesser amounts of chert, volcanic rocks, graywacke, and limestone (Cady and others, 1955). The Gemuk Group is interpreted to comprise part of a volcanic-arc complex (Box, 1985). Rocks of the Kuskokwim Group consist of thick sequences of intercalated sandstone and shale, with minor conglomerate and volcanic rocks (Cady and others, 1955; Miller and Bundtzen, 1994). The Kuskokwim Group consists primarily of deep-water turbidites and lesser shallow-shoreline-facies rocks (Miller and Bundtzen, 1994). Rocks of the Gemuk and Kuskokwim Groups are locally cut or overlain by Late Cretaceous and Tertiary intrusions and volcanic rocks. Mercury lodes in southwestern Alaska show a close spatial association to the Late Cretaceous and early Tertiary intrusions (Cady and others, 1955). The mercury lodes generally consist of small, discontinuous veins that rarely exceed a few meters in width and a few tens of meters in strike length. Mercury ores are geochemically simple, commonly containing over one percent each of Hg, Sb, and As, but are generally poor in base and precious metals. Most of the mercury lodes were located by tracing occurrences of placer cinnabar upstream to sources (Webber and others, 1947; Sainsbury and MacKevett, 1965). The lodes developed into mines were typically worked by a few individuals that operated small, on-site retorts.

At the Cinnabar Creek mine, sedimentary rocks of the Gemuk Group are cut locally by Late Cretaceous and Tertiary mafic dikes (Sainsbury and MacKevett, 1965). Mercury ores there are high grade and consist of massive replacements, disseminations, and vug fillings of cinnabar in quartz-carbonate veins that cut siltstone, graywacke, and an altered dike. At Cinnabar Creek, native mercury and lesser stibnite and pyrite are also found (Sainsbury and MacKevett, 1965). Native mercury is common in sheared and brecciated sedimentary rocks. The mine is located near the headwaters of Cinnabar Creek and consists of a small open-pit about 50 m long, 15 m wide, and 10 m deep. Ore averaging about 3 to 4 percent mercury was retorted on site, and several hundred flasks of mercury were recovered (Sainsbury and MacKevett, 1965). Veins containing cinnabar and native mercury in the open pit, and small ore piles at the mine site are sources of mercury that have eroded into Cinnabar Creek. Particulate (detrital) cinnabar grains and occasional beads of native mercury have been observed in stream-sediment samples collected from Cinnabar Creek (Gray and others, 1991).

The Red Top deposit is also underlain by sedimentary rocks of the Gemuk Group; a diabase dike of Late Cretaceous or early Tertiary age cuts the sedimentary rocks near the mine (Sainsbury and MacKevett, 1965). Cinnabar is found in quartz-carbonate veins and vein breccias that cut the sedimentary rocks. Mineralized veins and breccias are generally a few centimeters wide with maximum lengths of about 50 m. Ore was removed from underground workings and trenches totaling a few hundred meters in length. Ore containing greater than 2 percent mercury was reported from the mine (Webber and others, 1947), but only minor cinnabar is present in small ore piles near adit portals. Cinnabar retorted on site produced about 60 flasks of mercury (Sainsbury and MacKevett, 1965).

Rocks at the Mountain Top mine consist of sandstone and shale of the Kuskokwim Group that are cut locally by small Late Cretaceous and Tertiary mafic dikes (Sorg and Estlund, 1972). Vuggy, quartz-carbonate veins containing cinnabar are found in faulted and brecciated dikes that cut sedimentary rocks of the Kuskokwim Group. There are about 15 trenches that total roughly 500 m in length at Mountain Top; small ore piles with visible cinnabar are present near the trenches. Ore containing 1 to 2 percent mercury was reported from Mountain Top (Sorg and Estlund, 1972). About 165 flasks of mercury were recovered from this locality (Miller and others, 1989). Ore was presumably processed in a small retort found at the mine.

Rocks along the Kolmakof River site studied also consist of sandstone and shale of the Kuskokwim Group that are cut locally by small Late Cretaceous and Tertiary dikes (Cady and others, 1955). This site was selected for study because stream-sediment samples collected from an upstream tributary contain as much as 5.6 ppm Hg, and associated heavy-mineral-concentrate samples contain as much as 50 percent cinnabar (Gray and others, 1993). These results indicate the possible presence of undiscovered cinnabar lodes upstream, although none have been identified yet in this drainage basin.

Basins selected for background study on Boss Creek, Egozuk Creek, Holokuk River, Moose Creek, and Veahna Creek are underlain by sandstone and shale of the Kuskokwim Group that are cut locally by small Late Cretaceous and Tertiary intrusions (Cady and others, 1955; Miller and others, 1989). No cinnabar-bearing lodes or significant geochemical anomalies are known in these drainage basins.

## METHODS

### SAMPLE COLLECTION

Samples collected for study were primarily fish, but stream-sediment and stream-water samples were also col-

lected from most sites. All samples were collected from the active stream channel. Most fish were collected with spinning rods equipped with artificial lures, but those collected downstream from the Red Top mine were captured in gill net traps. Several fish (usually 5-10) were generally collected from a single site on a given stream or river; however, fish were collected from two sites on Chineekluk Creek downstream from the Mountain Top mine. The most commonly observed fish at the sites studied was Arctic grayling (*Thymallus arcticus*), and thus grayling represent the majority of the fish sampled. However, Dolly Varden (*Salvelinus malma*) were collected from some streams when grayling were rare or not present. Both Arctic grayling and Dolly Varden are freshwater fish that are common foods of residents and sportsmen in southwestern Alaska, and therefore they were appropriate to evaluate mercury contents in fish that are commonly consumed. Chum salmon (*Oncorhynchus keta*), coho salmon (*Oncorhynchus kisutch*), and northern pike (*Esox lucius*) are also common foods; these are migratory fish that were collected from large rivers in the study area to evaluate regional mercury hazards. Sculpin (*Scorpaena guttata*) were collected downstream from the Red Top mine to evaluate mercury concentrations in a bottom-feeding fish. Collected fish were dissected and muscle (edible fillets) and liver samples were saved for analysis. Muscle samples were analyzed for mercury because they are a common food source in the region. Livers generally concentrate heavy metals, and thus concentrations of mercury in livers help identify trends in the data. Sculpin collected were too small for dissection and were analyzed whole.

Stream-sediment samples were collected from stream-channel detritus for measurement of trace-metal concentrations. Collected stream-water samples included (1) an unfiltered sample collected in a glass bottle, acidified with nitric acid and potassium dichromate, for total mercury concentration; (2) a sample filtered through a 0.45- $\mu$ m membrane into a glass bottle, acidified with nitric acid and potassium dichromate, for dissolved mercury concentration; (3) an unfiltered sample collected in a polypropylene bottle, acidified with nitric acid, for other total trace-metal concentrations; and (4) a sample filtered through a 0.45- $\mu$ m membrane into a polypropylene bottle, acidified with nitric acid, for other dissolved trace-metal concentrations.

Stream-water pH, conductivity, alkalinity, and turbidity were also measured at the sites studied, but there was little variation in these measurements. The pH of the stream waters are neutral to slightly alkaline and varied between 7.1 and 8.4. These results are consistent with the mineralogy of the mercury deposits since cinnabar has an extremely low solubility in water (Hem, 1970) and does not readily form acid drainage because of its chemical and physical resistance during weathering. Thus, acid mine drainage downstream from abandoned mercury mines is probably not of environmental concern.

**Table 1.** Data for Arctic grayling (gyl) and Dolly Varden (doly) collected from background sites on Boss Creek (BS), Egozuk Creek (EZ), Holokuk River (HK), Moose Creek (MC), and Veahna Creek (VH)

[Analysis of Hg by cold-vapor atomic absorption spectrophotometry (CVAAS); Sb, As, Ag, Bi, Cd, Cu, Mo, Pb, and Zn by inductively coupled plasma-mass spectrometry (ICP-MS); fish weights are whole body measured on site; concentrations are in parts per million wet weight; n.d., not determined]

Sample	Tissue	Fish weight (g)	Hg ppm	Sb ppm	As ppm	Ag ppm	Bi ppm	Cd ppm	Cu ppm	Mo ppm	Pb ppm	Zn ppm
BS1gylM	muscle	260	0.14	<0.4	<0.4	<0.4	<0.7	<0.5	0.6	<0.4	<0.4	10
BS2gylM	muscle	255	.12	<.4	<.4	<.4	<.7	<.5	.6	<.4	<.4	9
BS3gylM	muscle	300	.14	<.4	<.4	<.4	<.7	<.5	.6	<.4	<.4	8
BS4gylM	muscle	325	.20	<.4	<.4	<.4	<.7	<.5	.6	<.4	<.4	8
BS5gylM	muscle	405	.17	<.4	<.4	<.4	<.7	<.5	.7	<.4	<.4	8
BS1gylL	liver	260	.19	<.4	<.4	<.4	<.7	<.5	2	<.4	<.4	21
BS2gylL	liver	255	.18	<.4	<.4	<.4	<.7	<.5	2	<.4	<.4	16
BS3gylL	liver	300	.20	<.4	<.4	<.4	<.7	<.5	2	<.4	<.4	20
BS4gylL	liver	325	.27	<.4	<.4	<.4	<.7	<.5	2	<.4	<.4	19
BS5gylL	liver	405	.18	<.4	<.4	<.4	<.7	<.5	2	<.4	<.4	12
EZ1gylM	muscle	500	.12	.01	.1	<.1	<.1	<.01	.4	<.01	.02	7
EZ2gylM	muscle	245	.08	<.01	<.1	<.1	<.1	<.01	.3	<.01	<.01	5
EZ3gylM	muscle	240	.09	<.01	.1	<.1	<.1	<.01	.5	<.01	<.01	5
EZ4gylM	muscle	190	.10	<.01	<.1	<.1	<.1	<.01	.3	<.01	<.01	6
EZ5gylM	muscle	520	.14	<.01	<.1	<.1	<.1	.01	.5	<.01	<.01	5
EZ6gylM	muscle	530	.13	<.01	.1	<.1	<.1	.01	.7	<.01	<.01	6
EZ1gylL	liver	500	.24	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	22
EZ2gylL	liver	245	.15	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	21
EZ3gylL	liver	240	.11	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	20
EZ4gylL	liver	190	.13	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	21
EZ5gylL	liver	520	.19	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	22
EZ6gylL	liver	530	.15	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	20
HK1gylM	muscle	310	.10	.02	<.1	<.1	<.1	.01	.4	<.01	.01	8
HK2gylM	muscle	350	.08	<.01	.1	<.1	<.1	<.01	.3	<.01	<.01	7
HK3gylM	muscle	300	.14	<.01	<.1	<.1	<.1	<.01	.3	<.01	<.01	5
HK4gylM	muscle	320	.12	<.01	<.1	<.1	<.1	<.01	.5	<.01	<.01	6
HK5gylM	muscle	420	.09	<.01	<.1	<.1	<.1	.01	.3	<.01	<.01	6
HK6gylM	muscle	305	.09	<.01	.1	<.1	<.1	<.01	.3	<.01	<.01	6
HK7gylM	muscle	230	.08	<.01	.1	<.1	<.1	<.01	.3	<.01	<.01	5
HK1gylL	liver	310	.10	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	21
HK2gylL	liver	350	.13	<.4	<.4	<.4	<.7	<.5	5	<.4	<.5	21
HK3gylL	liver	300	.13	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	18
HK4gylL	liver	320	.22	<.4	<.4	<.4	<.7	<.5	5	<.4	<.5	27
HK5gylL	liver	420	.14	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	22
HK6gylL	liver	305	.13	<.4	<.4	<.4	<.7	<.5	4	<.4	<.5	22
HK7gylL	liver	230	.08	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	13
MC1gylM	muscle	375	.16	<.01	<.1	<.1	<.1	<.01	.2	<.01	.02	6
MC1gylL	liver	375	.20	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	22
VH1gylM	muscle	110	.07	<.01	.1	<.1	<.1	<.01	.4	<.01	<.01	11
VH1dolyM	muscle	680	.14	<.01	1.2	<.1	<.1	<.01	1	<.01	<.01	5
VH2dolyM	muscle	55	<.02	.01	.1	<.1	<.1	<.01	.6	<.01	<.01	4
VH1gylL	liver	110	.11	<.4	.1	<.4	<.7	<.5	.8	<.4	<.5	10
VH1dolyL	liver	680	.01	<.4	.4	<.4	<.7	<.5	20	<.4	<.5	42

## ANALYTICAL METHODS

Mercury was measured in the fish samples using the cold-vapor atomic absorption spectrophotometry (CVAAS)

method of O'Leary (in press). Fish tissues were also analyzed for a multielement suite by an inductively coupled plasma-mass spectrometry (ICP-MS) technique modified from Meier and others (1994). All concentrations in fish are reported on a wet-weight basis (tables 1-4).

**Table 2.** Data for Dolly Varden (doly) and Arctic grayling (gyl) collected from Cinnabar Creek (CC), Chineekluk Creek (CHE-east site and CHW-west site), and the Kolmakof River (KF)

[Analysis of Hg by cold-vapor atomic absorption spectrophotometry (CVAAS); Sb, As, Ag, Bi, Cd, Cu, Mo, Pb, and Zn by inductively coupled plasma-mass spectrometry (ICP-MS); fish weights are whole body measured on site; concentrations are in parts per million wet weight; n.d., not determined]

Sample	Tissue	Fish weight (g)	Hg ppm	Sb ppm	As ppm	Ag ppm	Bi ppm	Cd ppm	Cu ppm	Mo ppm	Pb ppm	Zn ppm
CC1dolyM	muscle	230	0.62	0.01	0.1	<0.1	<0.1	<0.01	0.5	0.01	0.02	5
CC2dolyM	muscle	550	.23	.01	.1	<.1	<.1	<.01	.4	.01	.01	6
CC3dolyM	muscle	710	.08	<.01	.2	<.1	<.1	<.01	.3	<.01	.01	5
CC4dolyM	muscle	480	.43	.01	.1	<.1	<.1	<.01	.5	<.01	.02	6
CC1gylM	muscle	480	.15	<.01	.1	<.1	<.1	.01	.9	<.01	.01	7
CC1dolyL	liver	230	1.3	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	32
CC2dolyL	liver	550	.29	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	38
CC3dolyL	liver	710	.10	<.4	<.4	<.4	<.7	<.5	5	<.4	<.5	39
CC4dolyL	liver	480	.68	<.4	<.4	<.4	<.7	<.5	5	<.4	<.5	49
CC1gylL	liver	480	.26	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	26
CHE1gylM	muscle	355	.12	.01	.3	<.1	<.1	.01	.4	<.01	<.01	9
CHE2gylM	muscle	430	.26	.01	.2	<.1	<.1	.01	.4	<.01	<.01	5
CHW3gylM	muscle	230	.08	.01	.1	<.1	<.1	.01	.3	<.01	.01	5
CHW4gylM	muscle	305	.08	.01	.2	<.1	<.1	.01	.7	<.01	<.01	5
CHW5gylM	muscle	105	.07	.01	.2	<.1	<.1	.01	.6	<.01	<.01	6
CHE1gylL	liver	355	.16	<.4	<.4	<.4	<.7	<.5	3	<.4	<.5	23
CHE2gylL	liver	430	.35	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	21
CHW3gylL	liver	230	.15	<.4	<.4	<.4	<.7	<.5	4	<.4	<.5	25
CHW4gylL	liver	305	.13	<.4	<.4	<.4	<.7	<.5	4	<.4	<.5	24
CHW5gylL	liver	105	.13	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	20
KF1gylM	muscle	290	.09	.01	<.1	<.1	<.1	.01	.3	.01	.02	5
KF2gylM	muscle	315	.14	.01	<.1	<.1	<.1	.01	.4	.01	.01	5
KF3gylM	muscle	135	.08	.01	<.1	<.1	<.1	.01	.4	<.01	.03	6
KF4gylM	muscle	220	.10	.01	.1	<.1	<.1	.01	.3	.02	<.01	6
KF5gylM	muscle	140	.09	.01	.1	<.1	<.1	.01	.3	<.01	.04	5
KF6gylM	muscle	500	.42	.01	<.1	<.1	<.1	.01	.3	<.01	<.01	4
KF1gylL	liver	290	.24	<.4	<.4	<.4	<.7	<.5	3	<.4	<.5	23
KF2gylL	liver	315	.22	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	24
KF3gylL	liver	135	.14	<.4	<.4	<.4	<.7	<.5	1	<.4	<.5	20
KF4gylL	liver	220	.18	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	22
KF5gylL	liver	140	.16	<.4	<.4	<.4	<.7	<.5	2	<.4	<.5	20
KF6gylL	liver	500	.92	<.4	<.4	<.4	<.7	<.5	1	<.4	<.5	15

In the laboratory, stream-sediment samples were dried at temperatures below 50°C, sieved to minus-80 mesh, and pulverized. The sediments were analyzed for mercury by CVAAS following the technique of Kennedy and Crock (1987). Concentrations of Sb, As, Ag, Au, Bi, Cd, Cu, Mo, Pb, and Zn were determined in the stream-sediment samples by an inductively coupled plasma-atomic emission spectrometry (ICP-AES) technique (Motooka, 1988). The stream-water samples were also analyzed for Hg by CVAAS using a modified version of the technique of Kennedy and Crock (1987), and for Sb, As, Ag, Au, Bi, Cd, Cu, Mo, Pb, and Zn by ICP-MS (Meier and others, 1994). The analytical results for stream-sediment and stream-water samples are shown in table 5.

## RESULTS

### BACKGROUND SITES

Fish, stream-water, and stream-sediment samples were collected from several sites (fig. 1) to determine regional geochemical controls for this study. Arctic grayling collected from these sites contain mercury concentrations ranging from 0.07 to 0.20 ppm in muscle and 0.08 to 0.27 ppm in liver (table 1) and generally have low mercury concentrations relative to the other grayling collected in the study. Stream-water samples collected from background sites contain mercury concentrations below the 0.10 ppb lower limit of determination (table 5). These results are consistent with

**Table 3.** Data for sculpin and coho salmon collected downstream from the Red Top mine

[Analysis of Hg by cold-vapor atomic absorption spectrophotometry (CVAAS); fish weights are whole body measured on site; Hg concentrations are in parts per million wet weight]

Sample	Tissue	Fish weight (g)	Hg (ppm)
RTsculpA	whole body	6.9	0.06
RTsculpB	whole body	8.6	.06
RTsculpC	whole body	6.2	.02
RTsculpD	whole body	6.2	.05
RTsculpF	whole body	2.7	.02
RTsculpG	whole body	7.3	.02
RTsculpH	whole body	8.2	.03
RTsculpI	whole body	8.1	.03
RTsculpJ	whole body	5.2	.02
RTsculpK	whole body	5.9	.01
RTsculpL	whole body	6.9	.02
RTsculpM	whole body	5.4	.02
RTsculpN	whole body	5.3	.05
RTsculpO	whole body	2.8	.09
RTsculpP	whole body	6.7	.05
RTsculpQ	whole body	3.6	.04
RTsculpR	whole body	3.2	.06
RTsculpS	whole body	3.3	.12
RTsculpT	whole body	4.1	.02
RTsculpU	whole body	3.4	.10
RTcohoE	muscle	21	.08
RTcoho1A	muscle	11	.14
RTcoho1B	muscle	12	.08
RTcoho1C	muscle	9.3	.08
RTcoho1D	muscle	8.0	.03
RTcoho1E	muscle	11	.06
RTcoho1F	muscle	8.4	.06
RTcoho1G	muscle	5.3	.06
RTcoho1H	muscle	6.9	.03
RTcoho1I	muscle	6.4	.04

the low concentrations of mercury observed in natural surface waters, commonly less than 0.1 ppb (Wershaw, 1970). Other trace metals in the stream-water samples from background sites are also low and generally below limits of determination (table 5). Stream-sediment samples collected from background sites generally contain less than 0.5 ppm Hg. Mercury concentrations in fish, stream-water, and stream-sediment samples collected from these sites are similar, but slightly more variable, than those reported from other studies in the region (Crayton, 1990; Snyder-Conn and others, 1992; Gray and others, 1994).

### CINNABAR CREEK MINE

Fish collected from Cinnabar Creek, about 10 km downstream from the mine, contain the highest mercury concen-

trations in this study (table 2, fig. 2). Four Dolly Varden samples collected from Cinnabar Creek contain 0.08 to 0.62 ppm Hg in muscle and 0.10 to 1.3 ppm Hg in liver (table 2). One Arctic grayling collected from Cinnabar Creek in this study contains 0.15 ppm Hg in muscle and 0.26 ppm Hg in liver. The muscle sample of Dolly Varden containing 0.62 ppm Hg exceeds mercury concentrations in muscle samples of grayling (0.47 ppm) previously collected from Cinnabar Creek (Gray and others, 1994), but the fish collected for this study were larger (ranging from 230 to 710 g in weight) than the grayling collected by Gray and others (1994), which ranged from 9 to 45 g. In addition, Dolly Varden are higher in trophic position than grayling, and the higher mercury concentrations in the Dolly Varden are possibly a result of biomagnification. Dolly Varden are also migratory fish and probably feed along portions of the stream closer to the mine, where mercury concentrations are much higher. Other trace-metal concentrations in fish collected from Cinnabar Creek are considered low, and most are below analytical limits of determination (table 2).

The stream-sediment sample collected from Cinnabar Creek contains 1.0 ppm Hg, which is higher in mercury than the background sites (table 5). Previous studies have reported mercury concentrations in excess of 36 ppm in stream-sediment samples collected within about 7 km from the Cinnabar Creek mine (Gray and others, 1991). These results indicate that stream sediments in Cinnabar Creek contain abundant mercury.

The stream-water samples collected from Cinnabar Creek contain low concentrations of mercury and other trace metals. Mercury concentrations in the stream-water samples are 0.19 ppb (unfiltered) and <0.10 ppb (filtered). Antimony concentrations in the filtered stream-water sample were 0.4 ppb and 0.8 ppb in the unfiltered sample. All other trace metals in the stream-water samples are below analytical limits of determination. The presence of trace amounts of mercury and antimony in these stream waters is consistent with the presence of cinnabar, native mercury, and stibnite in the upstream Cinnabar Creek deposit.

### MOUNTAIN TOP MINE

The Mountain Top mine is located at the headwaters of a tributary of Chineekluk Creek, about 15 km upstream from the two collection sites (fig. 1). Five Arctic grayling collected from Chineekluk Creek contain mercury concentrations varying from 0.07 to 0.26 ppm in muscle and 0.13 to 0.35 ppm in liver (table 2). The grayling muscle containing 0.26 ppm Hg is slightly higher in mercury than grayling from background sites (fig. 2). The elevated mercury in the grayling suggests that, as in Cinnabar Creek, mercury from the Mountain Top deposit has been converted to a form of mercury (probably methylmercury) that is bioavailable to fish in Chineekluk Creek. Other trace-metal

**Table 4.** Data for chum salmon, coho salmon, and northern pike collected from the Kuskokwim River (AN-at Aniak, KR-at the Kolmakof mine, and SL-near Sleetmute) and the Holokuk River (HK)

[Analysis of Hg by cold-vapor atomic absorption spectrophotometry (CVAAS); Sb, As, Ag, Bi, Cd, Cu, Mo, Pb, and Zn by inductively coupled plasma-mass spectrometry (ICP-MS); fish weights are whole body wet weights measured on site; concentrations are in parts per million wet weight]

Sample	Tissue	Fish weight (kg)	Hg ppm	Sb ppm	As ppm	Ag ppm	Bi ppm	Cd ppm	Cu ppm	Mo ppm	Pb ppm	Zn ppm
AN1chumM	muscle	3.2	0.03	<0.4	0.4	<0.4	<1	<0.6	0.8	<0.5	<0.6	5
AN2chumM	muscle	3.2	.05	<.4	<.4	<.4	<1	<.6	.7	<.5	<.6	5
AN3chumM	muscle	3.1	.05	<.4	<.4	<.4	<1	<.6	<.7	<.5	<.6	4
AN4chumM	muscle	3.0	.04	<.4	.4	<.4	<1	<.6	.7	<.5	<.6	4
AN5chumM	muscle	1.8	.04	<.4	.6	<.4	<1	<.6	1	<.5	<.6	6
AN1chumL	liver	3.2	.04	<.4	<.4	.7	<1	1	30	<.5	<.6	24
AN2chumL	liver	3.2	.04	<.4	<.4	1	<1	1	47	<.5	<.6	24
AN3chumL	liver	3.1	.03	<.4	<.4	1	<1	1	71	<.5	<.6	93
AN4chumL	liver	3.0	.04	<.4	<.4	1	<1	1	91	<.5	<.6	29
AN5chumL	liver	1.8	.03	<.4	<.4	2	<1	3	64	<.5	<.6	28
HK1chumM	muscle	2.7	.06	<.4	.6	<.4	<1	<.6	2	<.5	<.6	8
HK2chumM	muscle	2.3	.08	<.4	<.4	<.4	<1	<.6	.9	<.5	<.6	9
HK1chumL	liver	2.7	.06	<.5	.7	3	<1	2	140	<.5	<.6	41
HK2chumL	liver	2.3	.05	<.5	<.4	3	<1	2	120	<.5	<.6	31
KRcoho1M	muscle	.92	.03	.01	.4	<.4	<1	<.6	.6	<.5	<.6	6
KRcoho1L	liver	.92	.04	<.4	<.4	<.4	<1	<.6	30	<.5	<.6	30
SL1pikeM	muscle	.75	.28	<.4	.2	<.4	<.1	<.1	.2	<.1	<.1	17
SL2pikeM	muscle	.98	.25	<.4	.3	<.4	<.1	<.1	.1	<.1	<.1	6
SL3pikeM	muscle	.96	.19	<.4	.3	<.4	<.1	<.1	.1	<.1	<.1	4
SL4pikeM	muscle	1.5	.31	<.4	.3	<.4	<.1	<.1	.2	<.1	<.1	5

concentrations in these fish are similar to those from background sites and are not of environmental concern.

Stream-sediment and stream-water samples were not collected from Chineekluk Creek for this study because such samples were previously collected about 5 km downstream from the Mountain Top mine (Gray and others, 1991). In the Gray and others (1991) study, mercury concentrations were 12 ppm in a stream-sediment sample and 0.10 ppb in a stream-water sample. Although these samples were collected about 10 km upstream from the site sampled in this study, the results indicate significant concentrations of mercury in the stream-sediment sample but low-level mercury concentrations in the stream-water sample.

#### KOLMAKOF RIVER

Fish, stream-sediment, and stream-water samples were collected from the Kolmakof River about 5 km downstream from a tributary where stream-sediment samples contain as much as 5.6 ppm Hg (Gray and others, 1993). No mercury lodes have been discovered in this drainage basin, perhaps because of the low, poorly exposed terrain. This site was selected for study because it represents an area where natu-

rally occurring mercury concentrations (baselines) can be reported prior to any mining. A stream-sediment sample collected from this site contains 5.7 ppm Hg, but the stream-water sample contained less than 0.10 ppb Hg (table 5). Six Arctic grayling collected from the Kolmakof River contain mercury concentrations from 0.08 to 0.42 ppm in muscle and 0.14 to 0.92 ppm in liver (table 2). The grayling containing 0.42 ppm Hg in muscle is elevated above mercury concentrations in fish muscle samples collected from background sites (fig. 2). Other trace-metal concentrations in fish, stream-sediment, and stream-water samples collected from the Kolmakof River are similar to those from background sites.

#### RED TOP MINE

Study of the Red Top mine was conducted in cooperation with Carol Outwater and Ward Jones, residents of Dillingham. Only fish were collected for this part of the study because equipment was not available for stream-sediment and stream-water sampling. Fish collected downstream from the Red Top mine contain low concentrations of mercury, ranging from 0.01 to 0.12 ppm in whole-body samples

**Table 5.** Geochemical data for stream-sediment and stream-water samples collected from Cinnabar Creek (CC), Kolmakof River (KF), Kuskokwim River (KR-at the Kolmakof mine and AN-near Aniak), Boss Creek (BS), Egozuk Creek (EZ), Holokuk River (HK), Moose Creek (MC), and Veahna Creek (VH)

[Analysis of Hg by cold-vapor atomic absorption spectrophotometry; Sb, As, Ag, Au, Bi, Cd, Cu, Mo, Pb, and Zn determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) in stream-sediment samples and by inductively coupled plasma-mass spectrometry (ICP-MS) in stream-water samples; concentrations for sediments are in parts per million (ppm) and for waters are in parts per billion (ppb); n.d., not determined; sample suffix RA, raw water; sample suffix FA, filtered water]

Sediments	Hg (ppm)	Sb (ppm)	As (ppm)	Ag (ppm)	Au (ppm)	Bi (ppm)	Cd (ppm)	Cu (ppm)	Mo (ppm)	Pb (ppm)	Zn (ppm)
CC4200S	1.0	1.9	16	<0.07	<0.1	<1.0	0.1	37	0.99	7.3	100
KF4304S	5.7	<1.0	6.1	<.07	<.1	<1.0	.1	14	.44	6.0	81
KR4306S	28	<1.0	6.6	<.07	<.1	<1.0	.2	27	.65	8.9	78
BS4301S*	.02	1.3	9.3	<.07	<.1	<1.0	.1	28	.65	10	110
EZ4302S*	.03	1.3	9.0	<.07	<.1	<1.0	.1	30	.71	9.5	110
HK4300S*	<.02	<1.0	8.3	<.07	<.1	<1.0	.1	32	1.0	8.6	110
MC4100S*	.33	10	5.4	<.07	<.1	<1.0	.08	17	.26	4.4	91
VH4303S*	.45	<1.0	11	<.07	<.1	<1.0	.1	17	.65	7.4	89
AN4308S*	.08	1.0	17	.21	.4	<1.0	.2	14	.94	8.7	67

waters	Hg (ppb)	Sb (ppb)	As (ppb)	Ag (ppb)	Au (ppb)	Bi (ppb)	Cd (ppb)	Cu (ppb)	Mo (ppb)	Pb (ppb)	Zn (ppb)	pH
CC4200RA	0.19	0.8	<2	<0.1	<0.1	<0.6	<1	<1	<0.4	<0.6	<2	7.1
CC4200FA	<.10	.4	<2	<.1	<.1	<.6	<1	<1	<.4	<.6	<2	
KF4304RA	<.10	.2	<2	<.1	<.1	<.6	<1	1	<.4	.9	9	7.5
KF4304FA	n.d.	<.2	<2	<.1	<.1	<.6	<1	.9	.2	<.6	<2	
KR4306RA	<.10	.3	<2	<.1	<.1	<.6	<1	2	.6	1	7	7.7
KR4306FA	n.d.	.2	<2	<.1	<.1	<.6	<1	.8	.7	<.6	<2	
BS4301RA*	<.10	<.2	<2	<.1	<.1	<.6	<1	<1	<.4	<.6	<2	7.1
BS4301FA*	<.10	<.2	<2	<.1	<.1	<.6	<1	<1	<.4	<.6	<2	
EZ4302RA*	<.10	<.2	<2	<.1	<.1	<.6	<1	<1	<.4	<.6	<2	8.4
EZ4302FA*	<.10	<.2	<2	<.1	<.1	<.6	<1	<1	<.4	<.6	<2	
HK4300RA*	<.10	<.2	<2	<.1	<.1	<.6	<1	<1	<.4	<.6	<2	7.4
HK4300FA*	<.10	<.2	<2	<.1	<.1	<.6	<1	<1	<.4	<.6	<2	
MC4100RA*	<.10	<.2	<2	<.1	<.1	<.6	<1	<1	<.4	<.6	<2	8.1
MC4100FA*	<.10	<.2	<2	<.1	<.1	<.6	<1	<1	<.4	<.6	<2	
VH4303RA*	<.10	<.2	<2	<.1	<.1	<.6	<1	1	<.4	<.6	<2	7.6
VH4303FA*	<.10	<.2	<2	<.1	<.1	<.6	<1	<1	<.4	<.6	<2	
AN4308RA*	<.10	<.2	<2	<.1	<.1	<.6	<1	<1	<.4	<.6	<2	7.1
AN4308FA*	<.10	<.2	<2	<.1	<.1	<.6	<1	2	<.4	<.6	<2	

\*Indicates background sites.

of sculpin, and from 0.03 to 0.14 ppm in muscle samples of coho salmon (table 3). These mercury concentrations are similar to those in fish collected from background sites throughout the region.

#### ADDITIONAL SITES

Sites along the Kuskokwim and Holokuk Rivers were studied to evaluate possible mercury bioaccumulation in fish that constitute major food sources. Salmon collected from the Kuskokwim and Holokuk Rivers have the lowest

concentrations of mercury in fish muscle samples collected in this study (table 4). Chum salmon collected from the Kuskokwim and Holokuk Rivers contain mercury concentrations ranging from 0.03 to 0.08 in muscle, and 0.03 to 0.06 in liver. Similarly, mercury in the stream-water and stream-sediment samples collected from these two sites is also low (table 5). One coho salmon collected from the Kuskokwim River adjacent to the Kolmakof mercury mine also contains low mercury concentrations, 0.03 ppm in muscle and 0.04 ppm in liver (table 4), even though the stream-sediment sample contains 28 ppm Hg. The high mercury concentration in this stream-sediment sample is a

result of erosion of cinnabar from the deposit into the stream channel at this site.

Northern pike (also a local food source) collected from the Kuskokwim River, about 4 km upstream from Sleetmute and about 12 km upstream from the Red Devil mine, contain mercury concentrations ranging from 0.19 to 0.31 ppm in muscle samples (table 4). Although these mercury concentrations are higher than those in background Arctic grayling and salmon collected in the region, they are much lower than mercury found in fish collected near the abandoned mercury mines. Pike are large, predatory fish (that is, higher in trophic position than grayling), and the mercury results for pike suggest some mercury biomagnification. Other trace-metal concentrations in the pike are not of environmental concern.

### INTERPRETATIONS

Some stream-sediment, stream-water, and fish samples collected below mercury mines contain mercury concentrations elevated above background values. A stream-water sample collected below the Cinnabar

Creek mine contains 0.19 ppb Hg, whereas background stream waters in the region typically contain less than 0.10 ppb Hg. Mercury concentrations in all stream-water samples is below both the 2-ppb drinking-water maximum-contaminant level recommended by the State of Alaska (Alaska Department of Environmental Conservation, 1994) and the 2.4 ppb maximum instream concentration recommended by the U.S. Environmental Protection Agency (EPA) (Environmental Protection Agency, 1992). However, mercury concentrations in some stream-water samples exceed the 0.012 ppb level that the EPA indicates may result in chronic effects to aquatic life. To evaluate possible aquatic life effects in the study area, edible portions of fish were analyzed to determine if mercury concentrations exceed the 1.0 ppm (wet weight) action level established by the Food and Drug Administration (FDA) (Federal Register, 1979).

Mercury concentrations in samples of freshwater fish collected downstream from the Cinnabar Creek and Mountain Top mercury mines, as well as those from the site on the Kolmakof River, exceed background values. Fish containing the highest mercury concentrations were 0.62 ppm in muscle and 1.3 ppm in liver samples from

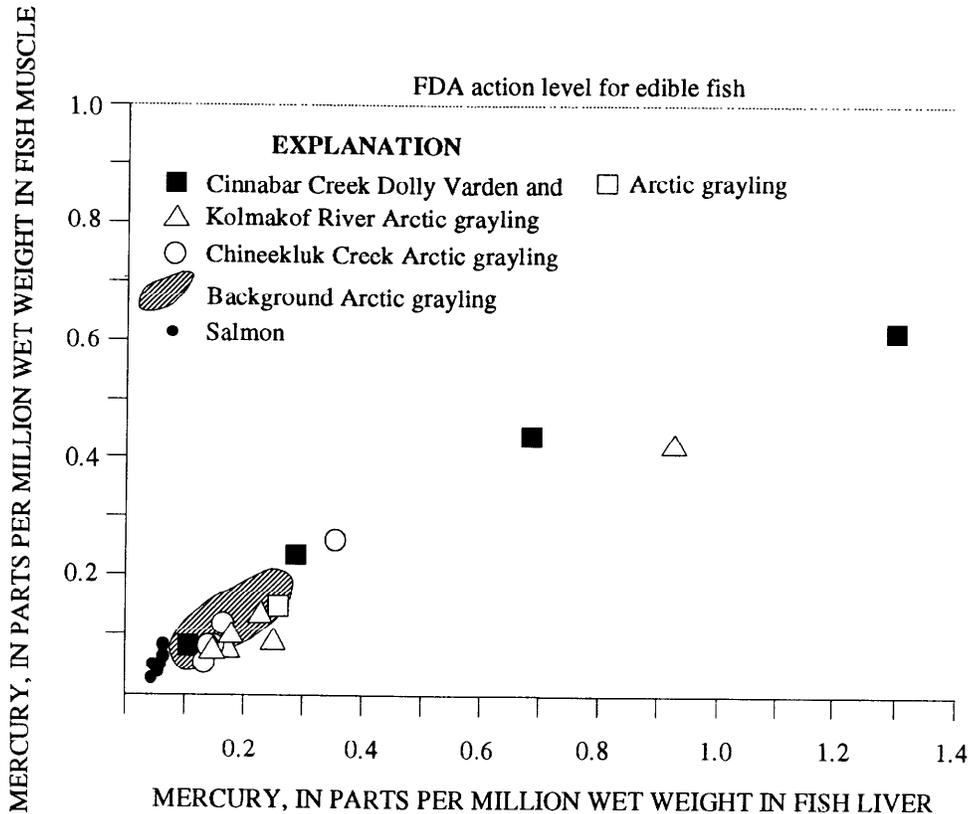


Figure 2. Plot of mercury in fish muscle versus mercury in fish liver from samples collected in this study.

Dolly Varden collected from Cinnabar Creek. Mercury concentrations as much as 0.47 ppm in muscle samples were also found in Arctic grayling collected from Cinnabar Creek (Gray and others, 1994). Mercury concentrations in the Dolly Varden and Arctic grayling collected from Cinnabar Creek are several times greater than those in fish collected from background sites in this study (fig. 2). Although the fish collected downstream from abandoned mercury mines and lodes contain elevated mercury concentrations in comparison to regional backgrounds, all mercury concentrations in samples of fish muscle are below the 1-ppm action level for edible fish established by the FDA. This is the concentration at which mercury advisories are listed and sale of fish is restricted by the FDA. A Dolly Varden liver sample collected from Cinnabar Creek contains 1.3 ppm Hg, but fish liver is not usually eaten by humans, and this concentration does not violate the FDA action level.

The elevated mercury concentrations in fish are interpreted to be a result of upstream mercury mines in the case of Cinnabar Creek and Mountain Top, and of undiscovered mercury lodes upstream from the site studied on the Kolmakof River. Mercury concentrations in these fish indicate that mercury introduced from the mines is bioavailable to the fish. In the stream environment, inorganic mercury (mostly cinnabar) is probably converted to organic mercury (methylmercury) and then passed onto fish through stream water, as well as through food sources such as invertebrate animals and other smaller fish that live in these streams. Such transfer of mercury to fish through food sources has been noted in freshwater ecosystems (Huckabee and others, 1979; Boudou and others, 1991). Mercury concentrations in water are low, even downstream from sources, because of the high volatility of mercury and its tendency to be sorbed by clays, microcrystalline oxides, sediment, and organic matter (Jenne, 1970). Although mercury concentrations in stream waters are generally less than 0.10 ppb, mercury is readily accumulated by fish when it is in a form that is biologically available in water.

Sculpin and coho salmon were collected downstream from the Red Top mine near Dillingham. Mercury concentrations in these fish were low, ranging from 0.01 to 0.12 ppm in samples of whole-body sculpin and 0.03 to 0.14 ppm in coho salmon muscle samples. These mercury concentrations are similar to those in freshwater fish reported in other studies (Crayton, 1990; Snyder-Conn and others, 1992; Gray and others, 1994). Results for the sculpin and coho salmon collected downstream from the Red Top mine suggest that (1) mercury has not had time to bioaccumulate because these fish are small and young; (2) there is little mercury in the stream environment, even though the stream drains a mercury mine; or (3) mercury in the stream draining the mine is not in a form that is biologically available to fish.

Salmon are an important subsistence and sport fish in southwestern Alaska, but salmon collected from the

Kuskokwim and Holokuk Rivers contain the lowest mercury concentrations of all the fish-muscle samples collected in this study. These results were not unexpected because salmon have a long ocean cycle and only return to freshwater streams and lakes for a short time to spawn. Northern pike (also a local food source) collected from the Kuskokwim River near Sleetmute contains mercury concentrations slightly elevated above background values but significantly lower than fish collected downstream from mercury mines. The salmon and pike were collected from large rivers and streams, and these data suggest that the influx of mercury from the naturally occurring mines and lodes is not large enough to adversely affect these fish. However, additional studies of salmon and pike need to be conducted because the sample population and distribution were not large enough to reach firm conclusions concerning mercury concentrations in these fish.

## SUMMARY

All concentrations of mercury in stream-water samples collected in this study are below the 2-ppb drinking-water maximum-contaminant level. Field measurements of pH indicate that stream waters draining mercury mines are neutral to slightly alkaline and are similar to background values. The dominant ore mineral in the mercury deposits is cinnabar, which is highly insoluble in water, resistant to physical and chemical weathering, and does not easily form acid drainage during weathering. Such near-neutral pH values are important because significant acid-drainage problems can result downstream from some sulfide-bearing mineral deposits and mines. However, acid formation in streams below the mercury mines in southwestern Alaska is probably insignificant environmentally.

Samples of muscle from Dolly Varden and Arctic grayling collected downstream from southwestern Alaska mercury mines and lodes contain mercury concentrations elevated above background values. The highest mercury concentration in fish is 0.62 ppm in a muscle sample and 1.3 ppm (wet weight) in a liver sample from a Dolly Varden collected below the Cinnabar Creek mine. However, all mercury concentrations in fish are below the 1 ppm wet-weight action level for edible fish established by the FDA as the concentration at which sale of fish is restricted.

Concentrations of mercury were also measured in salmon from large rivers to evaluate mercury levels in fish that constitute major food sources in the region. Chum salmon collected from the Kuskokwim and Holokuk Rivers contain the lowest mercury concentrations in muscle samples in the study, ranging from 0.03 to 0.08 ppm wet weight. Northern pike is another common food in the region, and samples collected from the Kuskokwim River near Sleetmute contain 0.19 to 0.31 ppm Hg wet weight in

muscle. All of these mercury concentrations are also well below the FDA action level.

Subsistence and sport fishing are common in southwestern Alaska, but the area is sparsely populated. The sites with the highest mercury concentrations in fish are distant from towns and unlikely to be frequent fishing sites. Mercury concentrations in fish collected in this study are below levels considered to be toxic to humans, but effects on organisms higher in the food chain remain to be addressed.

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