

# Geologic Studies in Alaska by the U.S. Geological Survey, 1995

Julie A. Dumoulin *and* John E. Gray, *Editors*

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Mercury in the  
terrestrial environment,  
Kuskokwim Mountains  
region, southwestern  
Alaska

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**COVER PHOTO:** Aerial view looking north across the Malaspina Glacier toward Mount Saint Elias (elevation 5,489 m), the third highest peak on the North American continent. Uplifted marine strata of Neogene age form the Samovar Hills in the foreground. Topographic relief in this area is dramatic (more than 4,800 vertical meters across less than 21 horizontal kilometers) and demonstrates rapid Neogene uplift and denudation (see article by O'Sullivan and others). Photograph by Austin Post.

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# Geologic Studies in Alaska by the U.S. Geological Survey, 1995<sup>1</sup>

By Julie A. Dumoulin *and* John E. Gray

## INTRODUCTION

This collection of 20 papers continues the annual series of U.S. Geological Survey (USGS) reports on geologic investigations in Alaska<sup>1</sup>. Contributions cover a broad spectrum of earth science topics and report results from all parts of the State (fig. 1).

USGS activities in Alaska include studies of environment and climate, hazards, resources, and geologic framework. Five papers in this volume discuss aspects of environment and climate. Environmental geochemistry of parts of southwestern and south-central Alaska is the focus of four articles; a fifth study, of emergent postglacial lake shorelines in southwestern Alaska, contributes to ongoing investigations of paleoclimate. Two papers address geologic hazards. The first assesses ground deformation in Katmai National Park at Novarupta dome, site of the largest volcanic eruption in this century, and the second evaluates earthquake risks related to the "Twin Peak fault" near Anchorage. Resources, including metallic minerals in northern, southwestern, and southeastern Alaska and coal in south-central Alaska, are discussed in four articles. Nine geologic framework studies apply a variety of techniques to a wide range of subjects throughout Alaska, including tectonics, geophysics, geochronology, biostratigraphy, sedimentology, paleogeography, and paleomagnetism.

Two bibliographies at the end of the volume list reports about Alaska in USGS publications released in 1995 and reports about Alaska by USGS authors in non-USGS publications in 1995.

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<sup>1</sup>This volume is the first to be published as a USGS Professional Paper. Prior volumes were published as USGS Bulletins (1988-1994) and USGS Circulars (1975-1987). The current title format was adopted for the 1985 volume; previous volumes were published under the title "The United States Geological Survey in Alaska: Accomplishments during 19\_\_."



Figure 1. Index map of Alaska showing 1:250,000-scale quadrangles and locations of study areas discussed in this bulletin.

# Mercury in the Terrestrial Environment, Kuskokwim Mountains Region, Southwestern Alaska

By Elizabeth A. Bailey and John E. Gray

## ABSTRACT

To evaluate environmental hazards of abandoned mercury mines in southwestern Alaska, mercury concentrations were measured in vegetation, soil, and stream-water samples collected from sites around the Cinnabar Creek and Red Devil mines, as well as from regional background sites. Mercury concentrations in all samples collected near the mines are elevated over those in background samples. Vegetation samples collected from the mines contain as much as 970 ppb Hg, whereas background vegetation samples contain no more than 190 ppb Hg. Soil samples collected from the mines contain as much as 1,500 ppm Hg, but background soil samples contain no more than 1.2 ppm Hg. In addition, concentrations of highly toxic methylmercury are low in samples of vegetation (no more than 37 ppb) and soil (no more than 133 ppb). Stream-water samples collected downstream from the mines contain no more than 0.28 ppb Hg and have nearly neutral pH values that range from 6.4 to 7.6. All stream-water mercury concentrations are well below the 2.0 ppb Hg drinking water standard recommended by the State of Alaska. Mercury concentrations in vegetation, soil, and stream-water samples collected from the Cinnabar Creek and Red Devil mines in this study are probably not hazardous to humans and wildlife in the region.

## INTRODUCTION

Mercury mines and deposits are found throughout southwestern Alaska (fig. 1); they represent significant sources of mercury that could potentially damage surrounding environments and may pose a potential health risk to residents and wildlife. As part of continuing mineral resource investigations in southwestern Alaska, the U.S. Geological Survey has been involved in assessing environmental mercury hazards in this region. Previous environmental studies have evaluated mercury contamination in fish collected downstream from mercury mines in the region to address effects to the aquatic food chain (Gray and others,

1994, 1996). Because mercury in aquatic systems can originate from terrestrial sources, such as mercury in mines, it is important to measure mercury concentrations in soil, water, and vegetation samples collected near such mines in order to better understand the behavior of mercury in both terrestrial and aquatic ecosystems. Certain vegetation species are important food sources for residents and wildlife in the region. Blueberries are consumed by humans and bears, alder twigs are eaten by ptarmigan, and willow leaves are an important food for moose. In this study, mercury concentrations were evaluated in vegetation, soil, and stream-water samples collected from the Cinnabar Creek and Red Devil mines. Variations in Hg concentration in different tissues of the same plant as well as between vegetation species were also investigated.

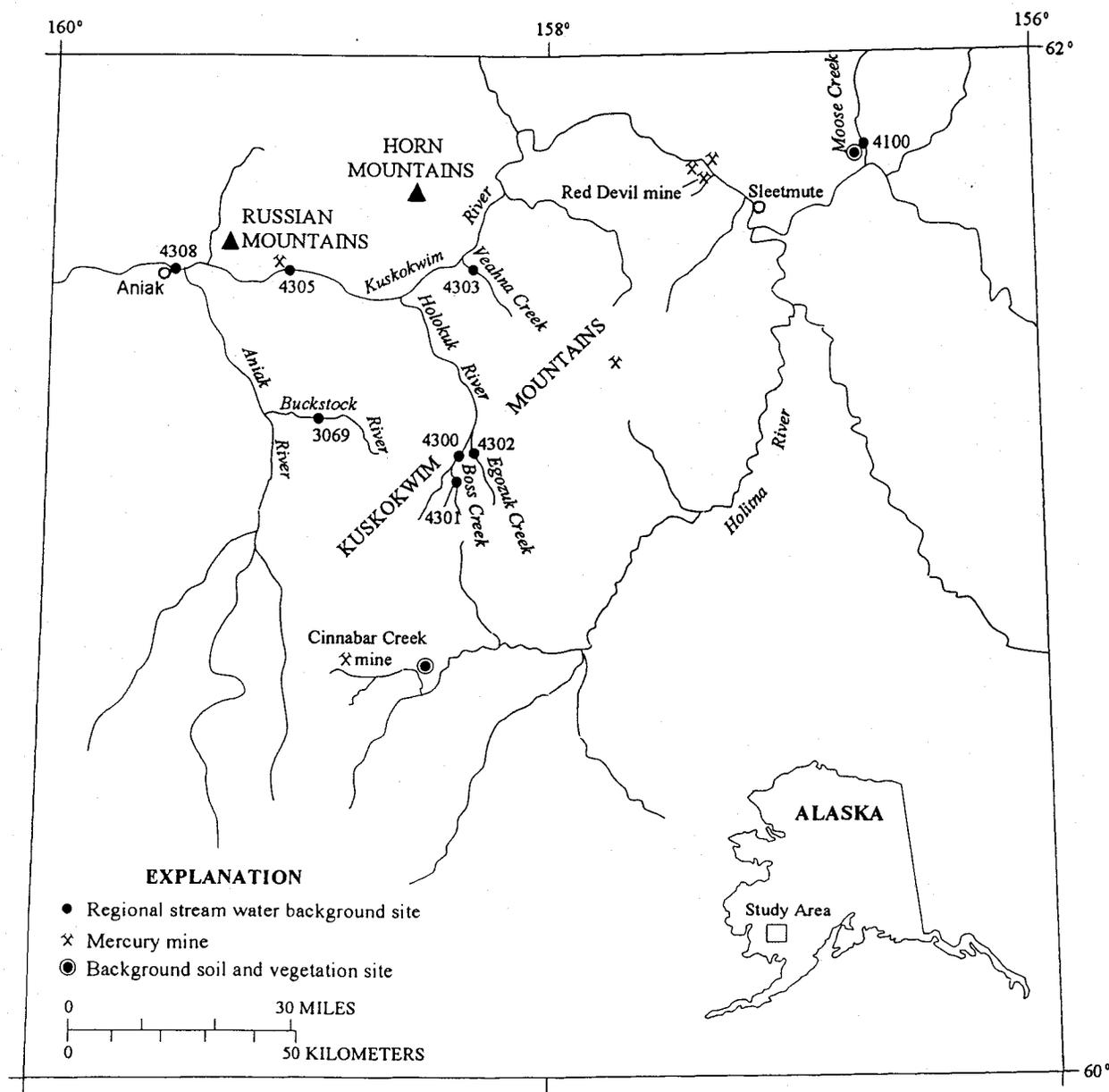
Mercury is a heavy metal with no known biological function in any organism. It comes in several forms, all of which are toxic to some degree (Agency for Toxic Substances and Disease Registry, 1994). When certain forms of Hg are ingested or inhaled by humans, the mercury adversely affects the central nervous system, the liver, and the kidneys; it can also cross the placental membrane in pregnant women, causing damage to the fetus (Clarkson, 1994). Mercury in the environment can be converted from inorganic forms such as HgS (cinnabar), Hg<sup>0</sup> (liquid mercury), or Hg<sup>2+</sup> (mercuric ion) to organic forms such as methylmercury (meHg) by aerobic and anaerobic bacteria. Organic mercury compounds, especially methylmercury, are the most toxic forms of mercury (Eisler, 1987). Methylmercury accumulates to a greater extent in biological tissues than do inorganic forms of mercury because of its affinity for the sulfhydryl (—SH) groups of some proteins (Agency for Toxic Substances and Disease Registry, 1994). Mercury concentrations increase in organisms that are higher in the food chain, a process called biomagnification. Concentrations of the organic forms of mercury in the terrestrial environment are generally at least one order of magnitude less than concentrations of inorganic forms of mercury, but in biological tissues methylmercury can constitute 70-100 percent of the total mercury concentration (Bloom, 1989; Baeyens, 1992; Gray and others, 1994).

## GEOLOGY

The Cinnabar Creek mine is located about 100 km southeast of Aniak in the southern Kuskokwim Mountains (fig. 1). Bedrocks in the area consist of interbedded graywacke, massive siltstone, volcanic rocks, and minor chert and limestone of the Triassic and Lower Cretaceous Gemuk Group (Cady and others, 1955; Sainsbury and MacKevett, 1965). Rocks of the Gemuk Group are locally cut by Late Cretaceous and early Tertiary mafic dikes (fig. 2) near the Cinnabar Creek mine.

Cinnabar was first discovered at Cinnabar Creek in 1941, and the mine operated intermittently from then until

1960 (Sainsbury and MacKevett, 1965). Mercury ore consists of massive replacements, disseminations, and vug fillings of cinnabar in quartz-carbonate veins (Sainsbury and MacKevett, 1965). Ore averaging about 3 to 4 percent mercury was retorted on site, and about 525 flasks (1 flask = 76 lb or 34.5 kg) of mercury were recovered (Nokleberg and others, 1987). 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. 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. Abundant cinnabar and a few beads of native mercury have been observed in stream-



**Figure 1.** Map of study area, showing locations of the Cinnabar Creek and Red Devil mines and of background sample sites. Several smaller mercury mines are also shown. Background samples were collected distant or upstream from known mines.

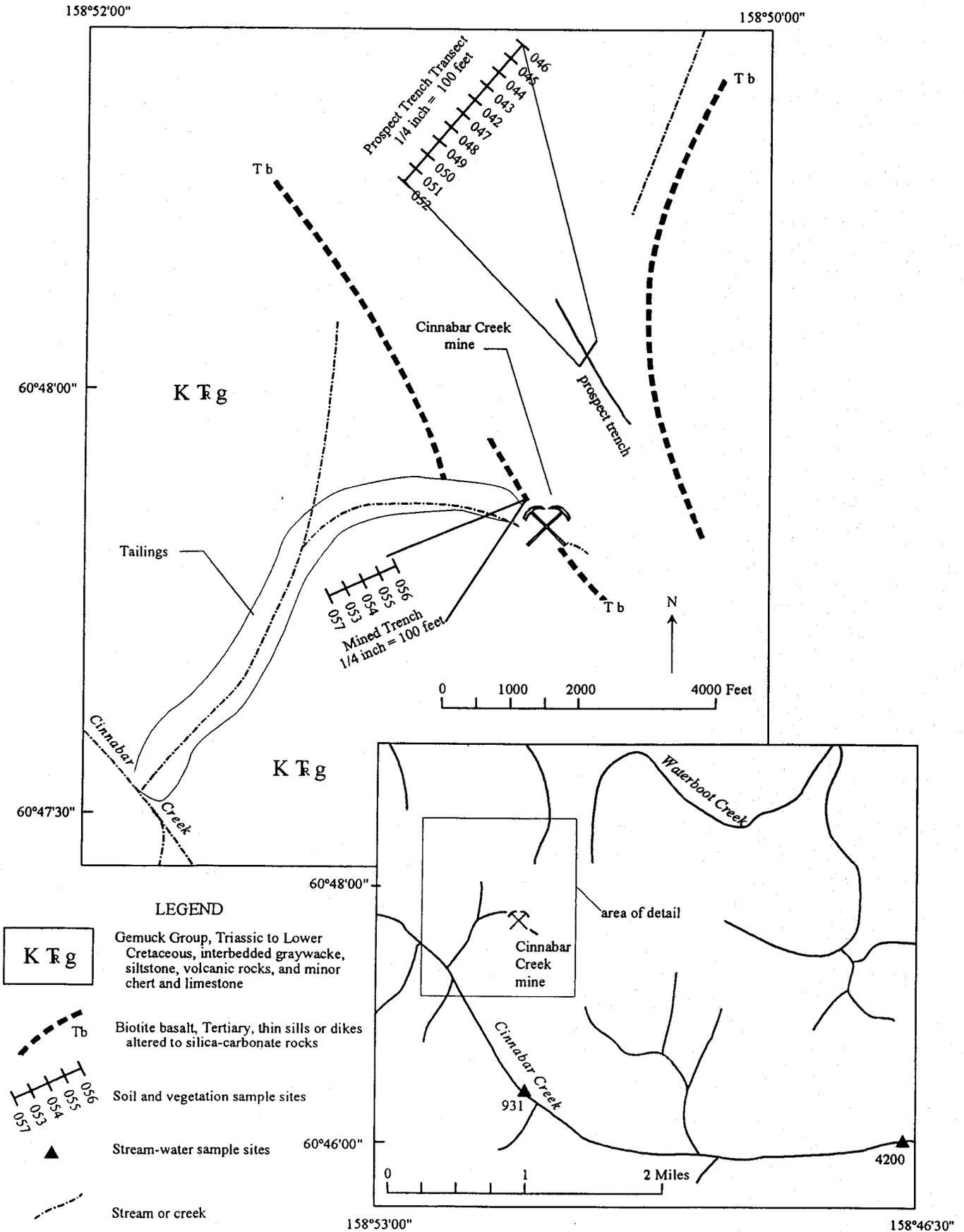


Figure 2. Sample locations and simplified geology, Cinnabar Creek mine. Geology generalized from Cady and others (1955).

sediment samples collected from Cinnabar Creek (Gray and others, 1991).

The Red Devil mine is located about 10 km northwest of the village of Sleetmute along the Kuskokwim River (fig. 1). Red Devil was Alaska's largest mercury mine; it operated intermittently from 1933 to 1971 and produced about 36,000 flasks of mercury (Miller and others, 1989). The deposit is found in rocks of the Cretaceous Kuskokwim Group (Cady and others, 1955), a thick sequence of interbedded graywacke and shale (fig. 3). These sedimentary rocks are cut locally by Late Cretaceous and early Tertiary dikes. Ore at Red Devil is in discontinuous open-space veins, vein breccias, and massive replacements localized along and near intersections between northeast-trending altered dikes and northwest-trending bedding plane faults (MacKevett and Berg, 1963). Principal metallic minerals are cinnabar and stibnite, with minor amounts of realgar, orpiment, and pyrite. Quartz, carbonate, dickite, and sericite are common gangue minerals (MacKevett and Berg, 1963).

The Red Devil mineralized zone covered an area about 150 m wide and 270 m long, which extended about 190 m vertically (MacKevett and Berg, 1963). Mineralized veins are mostly small, discontinuous, and less than 1 cm wide, but veins as much as 1 m wide and 10 m long were also observed (MacKevett and Berg, 1963). High-grade ore contained as much as 30 percent Hg, but most ore averaged about 2 to 5 percent Hg (Webber and others, 1947; MacKevett and Berg, 1963). Workings consisted of about 2,900 m of shafts, adits, drifts, crosscuts, and stopes (MacKevett and Berg, 1963), but the shafts and adits are presently caved. Numerous sloughed trenches total several hundred meters in length; most are heavily overgrown with alder and a few small spruce. Several ore and tailings piles on the site lie near the small Red Devil Creek that drains the mine area. The largest tailings pile is adjacent to the creek and is about 60 m wide and 75 m long. Abundant placer cinnabar and lesser stibnite are visible in Red Devil Creek.

## METHODS

### FIELD METHODS

At the Cinnabar Creek mine, vegetation and soil samples were collected at 15-m intervals along transects perpendicular to the mined trench and perpendicular to a prospect trench that had no recorded ore production (fig. 2). At the Red Devil mine, vegetation and soil samples were collected along a transect perpendicular to a large surface-mined area (fig. 3). Additional vegetation and soil samples were collected near the retort oven used during mining operations at Red Devil (fig. 3); no ore was actually mined from this area. The transects ranged from about 153 to 305 m long. Stream-water samples were also col-

lected from Cinnabar and Red Devil Creeks (figs. 2, 3) to evaluate mercury contamination in water downstream from the mines. To determine regional mercury background concentrations, vegetation, soil, and stream-water samples were collected from areas with geology similar to that of the mineralized areas, but where mercury deposits are not known (fig. 1).

Several vegetation samples were collected at each site. Species collected included alder (*Alnus crispa*), willow (*Salix* sp.), white spruce (*Picea glauca*), cottonwood (*Populus balsamifera*), black spruce (*Picea mariana*), blueberry (*Vaccinium uliginosum*), paper birch (*Betula papyrifera*), and dwarf birch (*Betula nana*). All of these plants are commonly found in the Kuskokwim Mountains region (Viereck and Little, 1972), but all species were not present at each site. A minimum of two plant species were collected at each site. For each vegetation sample, first-year growth material was collected—generally, the outermost 15 to 20 cm on the larger woody species and 8 to 10 cm on the shrub species.

Soil samples typically included the upper 15-20 cm of material just below the surface organic layer. This is the zone of most active root development and is generally the primary zone of mercury accumulation in forest soils (Godbold, 1994). In the study area, soils are usually poorly developed below about 15 cm.

At each water-collection site two samples were collected—one for dissolved Hg, and one for total Hg. Samples for total Hg were collected unfiltered in a glass bottle and were acidified with nitric acid and potassium dichromate. Samples for dissolved Hg were obtained by filtering the stream water through a 0.45- $\mu$ m membrane into a glass bottle and were then preserved with nitric acid and potassium dichromate. Stream-water pH, conductivity, and turbidity were also measured at each sample site.

### ANALYTICAL METHODS

In the laboratory, vegetation samples were washed two times with distilled deionized water to remove surface contamination. They were then dried at 40°C and separated into leaves, stems, and flowers or fruit tissues for separate analyses. Soil samples were dried at 40°C, sieved to minus-10 mesh, and then pulverized to minus-100 mesh. No further preparation was required for the stream-water samples.

All vegetation (tables 1, 2 and 4), soil (tables 3 and 4), and stream-water samples (table 5) were analyzed for total mercury concentration by the cold-vapor atomic-absorption spectrophotometry (CVAAS) method of O'Leary and others (1990). Stream-water data from Cinnabar Creek and some of the background sites are from Gray and others (1996). A subset of the vegetation and soil samples were analyzed for methylmercury by the cryogenic gas chroma-

tography cold-vapor atomic-fluorescence spectrometry (GC-AFS) method of Bloom (1989) and are reported in tables 1 through 4.

Soil pH and total organic carbon (TOC) are reported in tables 3 and 4. Soil pH was determined by adding equal

volumes of soil and distilled deionized water to a 100-mL beaker and mixing to form a slurry. When most of the material had settled, the pH of the mixture was measured using a digital pH meter. Soil TOC was determined by the method of Curry (1990).

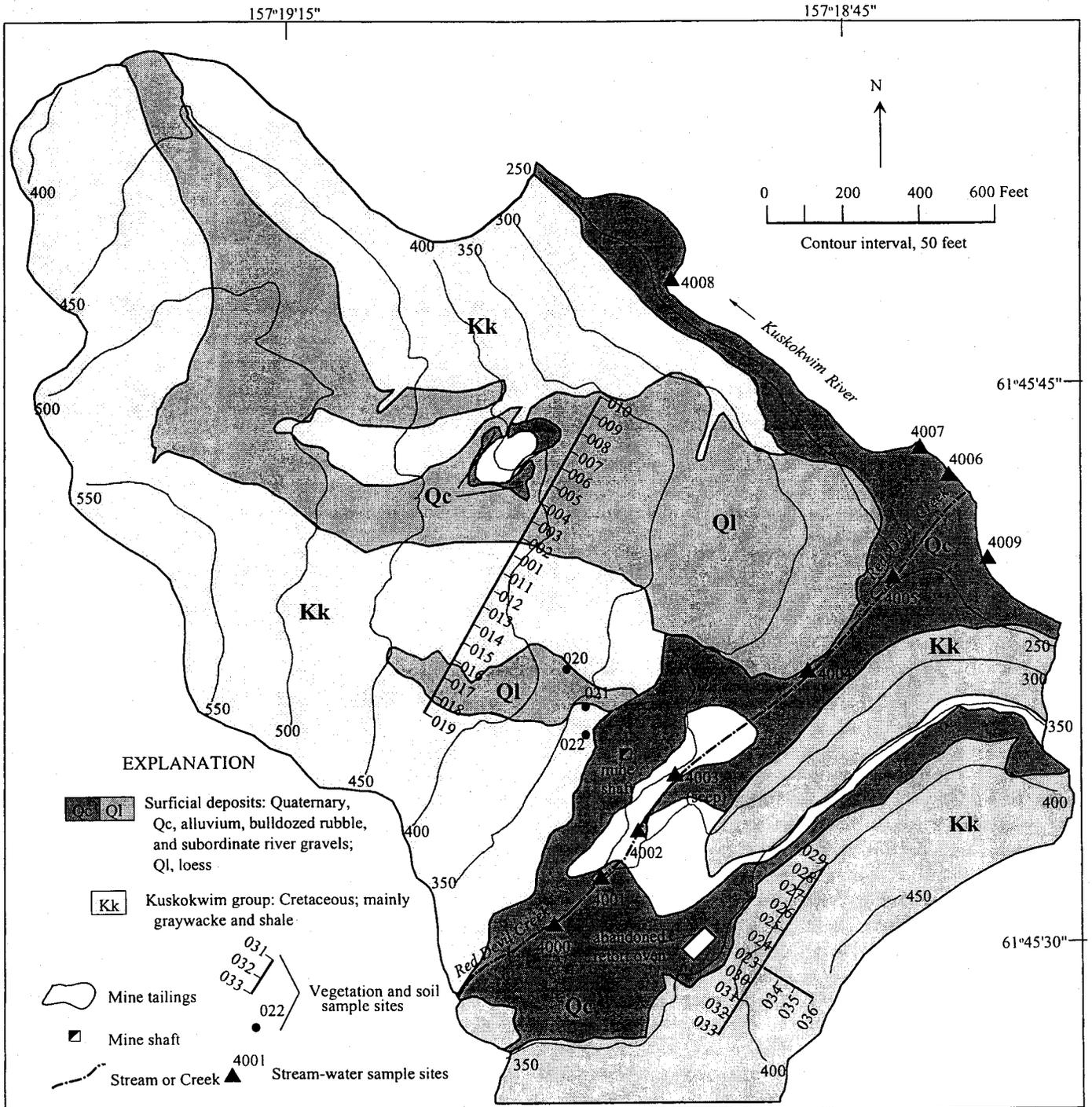


Figure 3. Sample locations and simplified geology, Red Devil mine. Geology generalized from MacKevett and Berg (1963).

**Table 1.** Geochemical data for vegetation samples collected at the Cinnabar Creek mine

[Analysis of total Hg by cold-vapor atomic-absorption spectrophotometry (CVAAS), lower limit of determination, 20 ppb; analysis of methylmercury (meHg) by cryogenic gas chromatography with atomic-fluorescence spectrometry; ppb, parts per billion; —, not determined or sample not collected; <, less than]

Field no.	A1 total Hg (ppb)	A1 meHg (ppb)	A2 total Hg (ppb)	A3 total Hg (ppb)	B1 total Hg (ppb)	B1 meHg (ppb)	B2 total Hg (ppb)	B2 meHg (ppb)	B3 total Hg (ppb)	C1 total Hg (ppb)	C2 total Hg (ppb)	E1 total Hg (ppb)	E2 total Hg (ppb)	F1 total Hg (ppb)	F1 meHg (ppb)	F2 total Hg (ppb)	F3 total Hg (ppb)	F3 meHg (ppb)	H1 total Hg (ppb)	H2 total Hg (ppb)	H3 total Hg (ppb)	total Hg (ppb)
Prospect area (unmined)																						
52	--	--	--	--	--	--	--	--	--	--	--	--	--	90	--	20	--	--	20	<20	50	
51	--	--	--	--	--	--	--	--	--	--	--	--	--	40	--	<20	--	--	40	<20	70	
50	40	--	<20	30	50	--	50	--	--	--	--	130	50	20	--	<20	--	--	--	--	--	
49	--	--	--	--	--	--	--	--	--	--	--	--	--	60	0.74	20	60	0.73	90	30	90	
48	130	--	<20	<20	40	--	40	--	--	20	<20	--	--	--	--	--	--	--	--	--	--	
42	250	1.04	50	140	100	36.7	150	26.2	310	--	--	--	--	--	--	--	--	--	--	--	--	
43	100	--	<20	20	30	--	30	--	--	--	--	--	--	--	--	--	--	--	--	--	--	
44	--	--	--	--	--	--	--	--	--	--	--	--	--	30	--	20	--	--	30	<20	100	
45	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	70	<20	40	
46	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	20	<20	30	
47	140	--	20	150	100	--	80	--	130	--	--	--	--	--	--	--	--	--	--	--	--	
Mined area																						
53	970	0.98	200	170	760	1.27	180	--	--	--	--	--	--	--	--	--	--	--	--	--	--	
54	250	--	30	80	670	--	50	--	270	--	--	--	--	--	--	--	--	--	--	--	--	
54D	240	--	40	120	580	--	50	--	180	--	--	--	--	--	--	--	--	--	--	--	--	
55	160	--	<20	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	
56	90	--	<20	--	850	--	40	--	--	--	--	--	--	--	--	--	--	--	--	--	--	
57	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	

<sup>1</sup> Codes for vegetation species and tissue type for tables 1 and 2:

A1: alder (*Alnus crispa*) leaves

A2: alder (*Alnus crispa*) stems

A3: alder (*Alnus crispa*) flowers

B1: willow (*Salix* sp.) leaves

B2: willow (*Salix* sp.) stems

B3: willow (*Salix* sp.) flowers

C1: white spruce (*Picea glauca*) needles

C2: white spruce (*Picea glauca*) stems

C3: white spruce (*Picea glauca*) cones

D1: cottonwood (*Populus balsamifera*) leaves

D2: cottonwood (*Populus balsamifera*) stems

D3: cottonwood (*Populus balsamifera*) flowers

E1: black spruce (*Picea mariana*) needles

E2: black spruce (*Picea mariana*) stems

E3: black spruce (*Picea mariana*) cones

F1: blueberry (*Vaccinium uliginosum*) leaves

F2: blueberry (*Vaccinium uliginosum*) stems

F3: blueberry (*Vaccinium uliginosum*) fruits

G1: paper birch (*Betula papyrifera*) leaves

G2: paper birch (*Betula papyrifera*) stems

G3: paper birch (*Betula papyrifera*) flowers

H1: dwarf birch (*Betula nana*) leaves

H2: dwarf birch (*Betula nana*) stems

H3: dwarf birch (*Betula nana*) flowers

## RESULTS

### BACKGROUNDS

Vegetation, soil, and stream-water samples were collected near the Red Devil and Cinnabar Creek mines to determine regional background mercury concentrations for this study (fig. 1). Alder was the only vegetation species present at both mines and at the background sites studied.

At the background site for the Red Devil mine (fig. 1, samples 37-40), total-mercury concentrations range from <20 to 100 ppb in alder leaves, from <20 to 30 ppb in alder stems, and from <20 to 150 ppb in alder flowers (table 4). At the background site for the Cinnabar Creek mine (fig. 1, samples 58-61), total-mercury concentrations range from 40 to 190 ppb in alder leaves, <20 to 20 ppb in alder stems, and 20 to 110 ppb in alder flowers (table 4). These results are consistent with earlier studies that found total-Hg concentrations of 6 to 100 ppb in vegetation collected from

areas where there is no mercury contamination (Siegal and others, 1985, 1987; Kovalevsky, 1987; Rasmussen and others, 1991); however, most of the previously published data are for total-mercury concentrations in whole plants and not for specific tissues such as leaves, stems, and fruit. Methylmercury concentrations measured in two alder leaf samples are 0.49 ppb (Red Devil, sample 39) and 0.45 ppb (Cinnabar Creek, sample 60).

Total Hg in soils collected from the Red Devil background sites range from 0.10 to 0.39 ppm (table 4), whereas soils collected from the Cinnabar Creek background sites contain 0.16 to 1.2 ppm total Hg (table 4). Methylmercury concentrations in soil samples collected at two background sites for Red Devil (sample 39) and Cinnabar Creek (sample 61) were 0.88 and 0.90 ppb, respectively. Soil pH values for all background samples are slightly acidic and range from 4.0 to 5.5, similar to values reported by Gough and others (1988). TOC ranges from 1.1 percent up to 10.7 percent, consistent with values generally found in poorly

Table 2. Geochemical data for vegetation samples collected at the Red Devil mine

[Analysis of total Hg by cold-vapor atomic-absorption spectrophotometry (CVAAS), lower limit of determination, 20 ppb; analysis of methylmercury (meHg) by cryogenic gas chromatography with atomic-fluorescence spectrometry; ppb, parts per billion; —, not determined or sample not collected; <, less than]

Field no.	A1 total Hg (ppb)	A1 meHg (ppb)	A2 total Hg (ppb)	A2 meHg (ppb)	A3 total Hg (ppb)	A3 meHg (ppb)	B1 total Hg (ppb)	B1 meHg (ppb)	B2 total Hg (ppb)	B3 total Hg (ppb)	C1 total Hg (ppb)	C2 total Hg (ppb)	C3 total Hg (ppb)	D1 total Hg (ppb)	D2 total Hg (ppb)	E1 total Hg (ppb)	E2 total Hg (ppb)	E3 total Hg (ppb)	F1 total Hg (ppb)	F1 meHg (ppb)	F2 total Hg (ppb)	F3 total Hg (ppb)	F3 meHg (ppb)	G1 total Hg (ppb)	G2 total Hg (ppb)	G3 total Hg (ppb)	
Retort area (unmined)																											
33	310	0.45	30	--	90	--	310	--	40	--	--	--	--	--	--	--	--	--	210	2.76	60	100	2.60	--	--	--	
32	--	--	--	--	--	--	330	--	90	--	--	--	--	--	--	--	--	--	330	--	90	--	--	--	180	70	--
31	--	--	--	--	--	--	280	--	60	--	--	--	--	--	--	210	210	--	260	--	70	70	--	--	--	--	--
30	--	--	--	--	--	--	150	--	50	--	--	--	--	--	--	--	--	--	180	--	120	70	--	--	140	40	90
23	--	--	--	--	--	--	180	--	70	--	--	--	--	--	--	--	--	--	190	--	50	40	--	--	160	40	--
24	--	--	--	--	--	--	180	--	30	--	--	--	--	--	--	150	150	370	230	--	50	100	--	--	--	--	--
25	--	--	--	--	--	--	160	--	40	--	--	--	--	--	--	90	40	100	230	--	70	80	--	--	100	30	120
26	--	--	--	--	--	--	180	--	40	260	--	--	--	--	--	110	110	160	160	--	50	40	--	--	--	--	--
27	--	--	--	--	--	--	130	--	90	--	--	--	--	--	--	90	100	60	110	--	40	30	--	--	--	--	--
28	--	--	--	--	--	--	90	--	40	310	--	--	--	--	--	70	60	50	80	--	30	40	--	--	--	--	--
29	--	--	--	--	--	--	160	--	30	--	--	--	--	--	--	70	80	210	80	--	40	60	--	--	--	--	--
34	--	--	--	--	--	--	180	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
35	--	--	--	--	--	--	140	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
36	--	--	--	--	--	--	90	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Mined area																											
19	--	--	--	--	--	--	100	--	30	--	--	--	--	--	--	30	100	20	40	--	<20	50	--	40	<20	--	--
18	--	--	--	--	--	--	380	--	70	--	60	20	30	--	--	--	--	--	60	--	30	40	--	130	30	40	--
17	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	150	--	70	--	--	--	--	--	--
16	--	--	--	--	--	--	40	--	<20	--	--	--	--	--	--	70	<20	200	30	--	<20	60	--	30	<20	--	--
15	50	--	<20	--	30	--	--	--	--	--	--	--	--	--	--	20	40	60	--	--	--	--	--	--	--	--	--
14	40	--	<20	--	30	--	--	--	--	--	--	--	--	180	30	--	--	--	--	--	--	--	--	--	--	--	--
13	30	--	<20	--	<20	--	--	--	--	--	60	90	--	280	20	--	--	--	--	--	--	--	--	--	--	--	--
12	80	--	20	--	30	--	150	--	30	--	50	60	--	60	30	--	--	--	--	--	--	--	--	--	--	--	--
11	60	--	<20	--	30	--	--	--	--	--	--	--	--	100	40	--	--	--	--	--	--	--	--	--	--	--	--
1	150	0.72	30	0.80	40	0.87	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
2	900	0.54	40	--	40	--	560	2.73	70	--	140	130	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3	90	--	20	--	40	--	210	--	30	--	130	70	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
4	100	--	30	--	50	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
5	120	--	30	--	50	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
6	320	--	20	--	60	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
7	80	--	<20	--	<20	--	100	--	40	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
8	40	--	<20	--	30	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
9	110	--	<20	--	40	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
10	40	--	<20	--	<20	--	100	--	20	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
20	120	--	30	--	30	--	130	--	50	--	--	--	--	160	40	--	--	--	--	--	--	--	--	--	--	--	--
21	300	--	30	--	60	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
22	420	--	50	--	120	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

See table 1 for explanation of codes for vegetation species and tissue types.

drained boreal (northern) forest soils (Brady and Weil, 1996).

Background stream-water samples were collected from two sites upstream from the Red Devil mine and at several sites throughout the Kuskokwim River region (fig. 1). All stream-water samples collected from background sites contain less than 0.1 ppb Hg (table 5). These results are consistent with the low concentrations of mercury observed in natural surface waters, which are commonly less than 0.1 ppb (Wershaw, 1970). The pH of background stream waters are near neutral to slightly alkaline and range from 6.8 to 8.4. Conductivity values in samples collected from background sites range from 60 to 115 µS/cm. Turbidity, a

measure of suspended matter such as clay, organics, and microorganisms, is generally low at most sites in streams measured for background in the region and ranges from 2 to 6 nephelometric turbidity units (NTU) at most sites; these values are similar to the 5-NTU State of Alaska drinking water standard (Alaska Department of Environmental Conservation, 1994). Turbidity measurements were somewhat higher on Red Devil Creek; for example, turbidity was 15 NTU in a small seep near the mine (table 5, sample RD4003). Turbidity as high as 30 NTU (table 5, sample KF4305) was measured on the Kuskokwim River and is probably related to suspended, glacially derived material in upstream tributaries that originate in the Alaska Range.



**Table 5.** Geochemical data for stream-water samples collected from the Red Devil mine, Cinnabar Creek mine, and background sites in the Kuskowkim River region

[Analysis of Hg by cold-vapor atomic-absorption spectrophotometry (CVAAS), lower limit of determination, 0.10 ppb; ppb, parts per billion; NTU, nephelometric turbidity units; RA, raw unfiltered water sample; FA, filtered water sample; —, not determined or sample not collected; <, less than]

Sample	Locality	Hg (ppb)	pH	Conductivity ( $\mu$ S/cm)	Turbidity (NTU)
RD4002RA	Red Devil	0.14	7.4	100	3.5
RD4002FA	Red Devil	<.10	--	--	--
RD4003RA	Red Devil	<.10	6.4	275	15
RD4003FA	Red Devil	<.10	--	--	--
RD4004RA	Red Devil	.28	7.1	115	3.5
RD4004FA	Red Devil	<.10	--	--	--
RD4005RA	Red Devil	.26	7.0	115	3.5
RD4005FA	Red Devil	<.10	--	--	--
RD4006RA	Red Devil	<.10	7.2	80	8.5
RD4006FA	Red Devil	<.10	--	--	--
RD4007RA	Red Devil	.16	7.4	80	8.5
RD4007FA	Red Devil	<.10	--	--	--
RD4008RA	Red Devil	<.10	7.5	80	8.5
RD4008FA	Red Devil	<.10	--	--	--
RD4009RA	Red Devil	.19	7.6	75	8.0
CC4200RA	Cinnabar Creek	.19	7.1	65	5.0
CC4200FA	Cinnabar Creek	<.10	--	--	--
CC931FA	Cinnabar Creek	<.10	6.4	190	--
Background sites					
RD4000RA	Red Devil	<0.10	7.6	105	3.5
RD4000FA	Red Devil	<.10	--	--	--
RD4001RA	Red Devil	<.10	7.6	105	2.0
RD4001FA	Red Devil	<.10	--	--	--
MC4100RA	Moose Creek	<.10	8.1	75	4.0
MC4100FA	Moose Creek	<.10	--	--	--
HK4300RA	Holokuk River	<.10	7.3	95	6.0
HK4300FA	Holokuk River	<.10	--	--	--
BS4301RA	Boss Creek	<.10	7.1	60	4.0
BS4301FA	Boss Creek	<.10	--	--	--
EZ4302RA	Egozuk Creek	<.10	8.4	80	4.5
EZ4302FA	Egozuk Creek	<.10	--	--	--
VH4303RA	Veahna Creek	<.10	7.6	75	5.0
VH4303FA	Veahna Creek	<.10	--	--	--
KF4305RA	Kuskokwim River	<.10	7.7	115	30
KF4305FA	Kuskokwim River	<.10	--	--	--
AN4308RA	Kuskokwim River	<.10	7.1	60	15
AN4308FA	Kuskokwim River	<.10	--	--	--
BR3069FA	Buckstock River	<.10	6.8	60	--

### CINNABAR CREEK

At the Cinnabar Creek mine, total-mercury concentrations in vegetation samples collected range from 20 to 970 ppb in leaves and needles, <20 to 200 ppb in stems, and <20 to 310 ppb in flowers (table 1). Leaf samples collected

from Cinnabar Creek contain methylmercury concentrations ranging from 0.73 to 36.7 ppb (table 1).

Soil samples collected from the Cinnabar Creek mine contain from 0.13 to 1,500 ppm total Hg, with a mean of 157 ppm (table 3). Mine-site soil samples contain from 5.03 to 133 ppb methylmercury (table 3). The soils are

slightly acidic to slightly alkaline; they range from pH 4.5 to 7.6 and have a mean pH of 5.0. Mean TOC content is 3.87 percent but ranges from 0.44 to 4.95 percent (table 3).

Mercury concentrations are slightly elevated in the raw unfiltered stream-water samples collected from Cinnabar Creek downstream from the main mine trench (0.19 ppb), but the filtered stream-water samples contained less than 0.10 ppb, similar to mercury concentrations in the stream-water samples collected from background sites (table 5). Stream-water samples collected from Cinnabar Creek had near neutral pH (6.4 and 7.1) and low conductivity (65 and 190  $\mu\text{S}/\text{cm}$ ) and turbidity values (5.0 NTU), similar to those measured at Red Devil Creek (table 5).

## RED DEVIL

At the Red Devil mine, total-mercury concentrations in all vegetation samples collected range from 20 to 900 ppb in leaves, <20 to 210 ppb in stems, and <20 to 370 ppb in flowers (table 2). Leaf samples analyzed for methylmercury have concentrations ranging from 0.45 to 2.76 ppb (table 2).

In the soil samples collected from the Red Devil mine, total-mercury concentrations range from 0.05 to 1,200 ppm, with a mean of 82 ppm (table 3). Soil methylmercury concentrations in samples from Red Devil range from 2.7 to 8.2 ppb (table 3). Soil pH ranges from 4.1 to 6.8, with a mean of 5.2. The average TOC content is 2.66 percent but ranges from 0.30 to 8.99 percent (table 3).

Stream-water samples collected in Red Devil Creek downstream from the mine contain as much as 0.28 ppb Hg in raw unfiltered stream-water samples. However, in all filtered water samples collected downstream from the mines, Hg concentrations are less than 0.10 ppb and similar to mercury concentrations in stream-water samples collected from background sites (table 5). The pH of the stream-water samples collected from the Red Devil mine varies between 6.4 and 7.6 (table 5). Conductivity values in samples collected downstream from the Red Devil mine range from 75 to 115  $\mu\text{S}/\text{cm}$ , with the exception of a water sample (RD4003) collected from a seep draining a caved adit at Red Devil that has a conductivity of 275  $\mu\text{S}/\text{cm}$  (table 5). In samples collected downstream from the mine, turbidity varies from 3.5 to 8.5 NTU, again with the exception of sample RD4003, which has a turbidity of 15 NTU (table 5).

## DISCUSSION

### VEGETATION SAMPLES

#### MERCURY VARIATIONS IN PLANT TISSUE TYPES

In all vegetation samples, total-mercury concentrations are generally highest in the leaves and lowest in the stems

(figs. 4, 5). Some plant tissues have a greater ability to absorb mercury than others (Kabata-Pendias and Pendias, 1992), but the data do not always clearly identify which plant tissues most readily absorb mercury (Warren and others, 1983; Kovalevsky, 1987; Rasmussen and others, 1991; Lodenius, 1994). Some studies suggest discarding stem tissue because stems generally contain low mercury concentrations (Rasmussen and others, 1991). Results of our study support this conclusion. However, Kovalevsky (1987) found that stems of some Siberian conifers contain higher mercury concentrations than do other parts of the plant. Lodenius (1994) reported that mercury concentrations are generally lower in the flowers and leaves than in other parts of plants. Warren and others (1983) found that in over 100 species collected from the Pinchi Lake mercury mine area in British Columbia, roots and flowers tended to have higher concentrations of mercury than did first-year leaves and first- or second-year stems. Our study suggests that leaves tend to concentrate mercury to a greater extent than do stems or flowers.

#### MERCURY VARIATIONS BETWEEN VEGETATION SPECIES

Plant species differ in their ability to take up mercury, as can be seen in the considerable variation between the species we sampled (figs. 4, 5). At the Red Devil and Cinnabar Creek mines, alders and willows concentrate mercury at levels as much as 20 times higher than those in the other species collected in this study. Data from Warren and others (1983) support this observation. The mechanism of mercury uptake and why certain species accumulate more mercury than others is unclear. Siegal and others (1985, 1987) suggested that some species are mercury accumulators, whereas other plant species reject mercury, or possibly that certain plants release their absorbed mercury as mercury vapor ( $\text{Hg}^0$ ) and thus lower their total concentration of mercury.

#### MERCURY IN VEGETATION—MINES VERSUS BACKGROUNDS

Total-mercury concentrations in alder samples are much higher in the mine-site samples than in the background samples (figs. 4, 5). Alder leaves collected near the mines contain mercury concentrations that range from 30 to 970 ppb. These values are similar to concentrations (28 to 1,150 ppb) measured by Warren and others (1966) and Siegal and others (1985) in various species collected near the Pinchi Lake mercury mine, but most of these values are for whole plants, not specific tissues. Alder leaves collected from background sites for our study contain from <20 to 100 ppb mercury at Red Devil and from 40 to 190 ppb mercury at Cinnabar Creek; these values are similar to worldwide background values in vegetation of 3 to 100 ppb reported by Lodenius (1994).

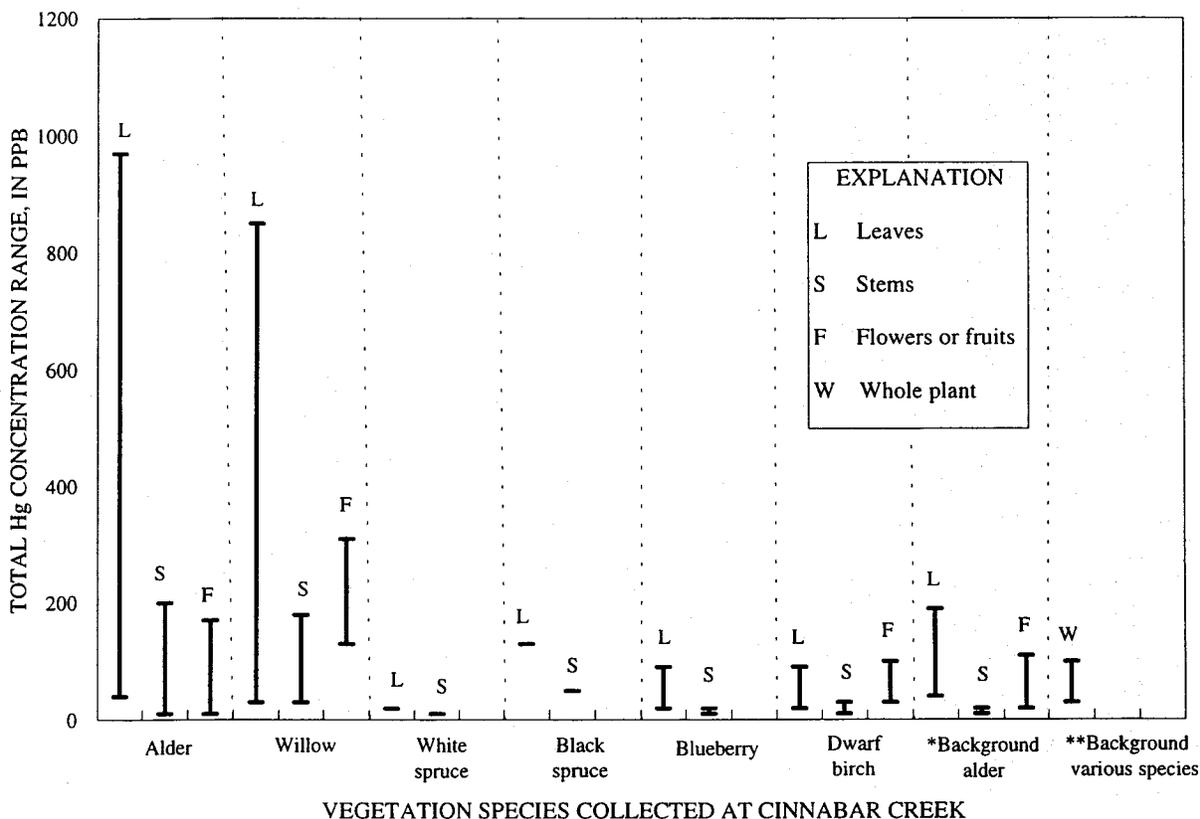


Figure 4. Variation in total-mercury concentrations (in parts per billion) between vegetation species sampled and between tissue type at the Cinnabar Creek mine. The single asterisk denotes background data from this study; the double asterisk represents background data from Rasmussen and others (1991), Siegal and others (1985), and Warren and others (1983).

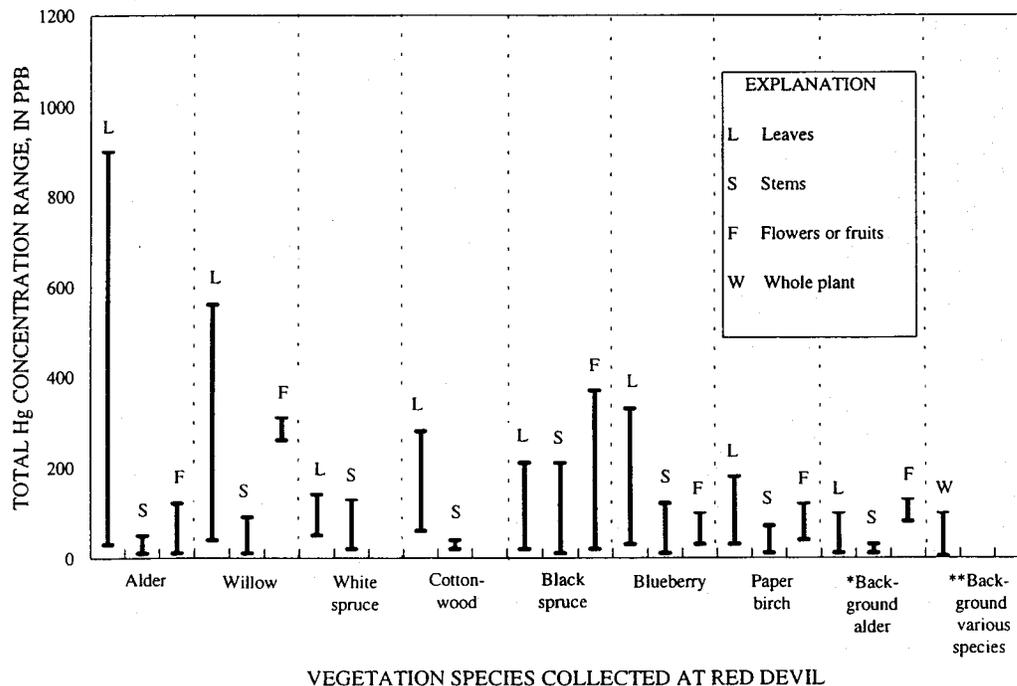


Figure 5. Variation in total-mercury concentrations (in parts per billion) between vegetation species sampled and between tissue type at the Red Devil mine. The single asterisk denotes background data from this study; the double asterisk represents data from Rasmussen and others (1991), Siegal and others (1985), and Warren and others (1983).

## SOIL SAMPLES

## SOIL MERCURY—MINES VERSUS BACKGROUNDS

Not surprisingly, total-mercury concentrations are significantly higher in soil samples collected from both the Red Devil and Cinnabar Creek mines (as much as 1,500 ppm) than in samples collected at the background sites (0.10 to 1.2 ppm, fig. 6). These elevated mercury concentrations in soils are somewhat higher than the values (14 to 500 ppm) found by other studies of abandoned mercury mines in British Columbia (Warren and others, 1966; Siegal and others, 1985) but are not substantially different. Most of the mercury present in soils at these abandoned mines probably occurs as cinnabar. It is the most stable form of mercury at the pH levels observed in these soils (Andersson, 1979).

We found somewhat higher background levels of mercury in soils (0.10 to 1.2 ppm) than those reported from organic-rich soils in other areas. For example, in Norway and Sweden, background mercury concentrations reported from organic-rich forest soils are less than 0.24 ppm

(Lindqvist, 1991). In the United States, mean concentrations reported from organic soils and loamy soils are 0.28 ppm Hg and 0.13 ppm Hg, respectively (Kabata-Pendias and Pendias, 1992). Background levels for organic soils in Canada as high as 0.40 ppm Hg are reported (Kabata-Pendias and Pendias, 1992). Shacklette and Boerngen (1984) report an average value of 0.058 ppm total Hg for background concentration in all soil types in the conterminous United States. The higher concentrations of mercury in soils sampled for background measurements in our study may indicate high regional background levels of mercury.

Methylmercury concentrations, like total-mercury concentrations, are higher in the mine-site soils in our study area (2.73 to 133 ppb; table 3) than in the background samples (0.88 to 0.90 ppb; table 4). In addition, methylmercury concentrations in soil samples collected from the Cinnabar Creek and Red Devil mines are as much as 50 times higher than the average background concentration of 2.5 ppb reported for sediments worldwide by Baeyens (1992), but the average methylmercury concentration for background soils collected in our study (0.89 ppb) is much lower than this worldwide average value.

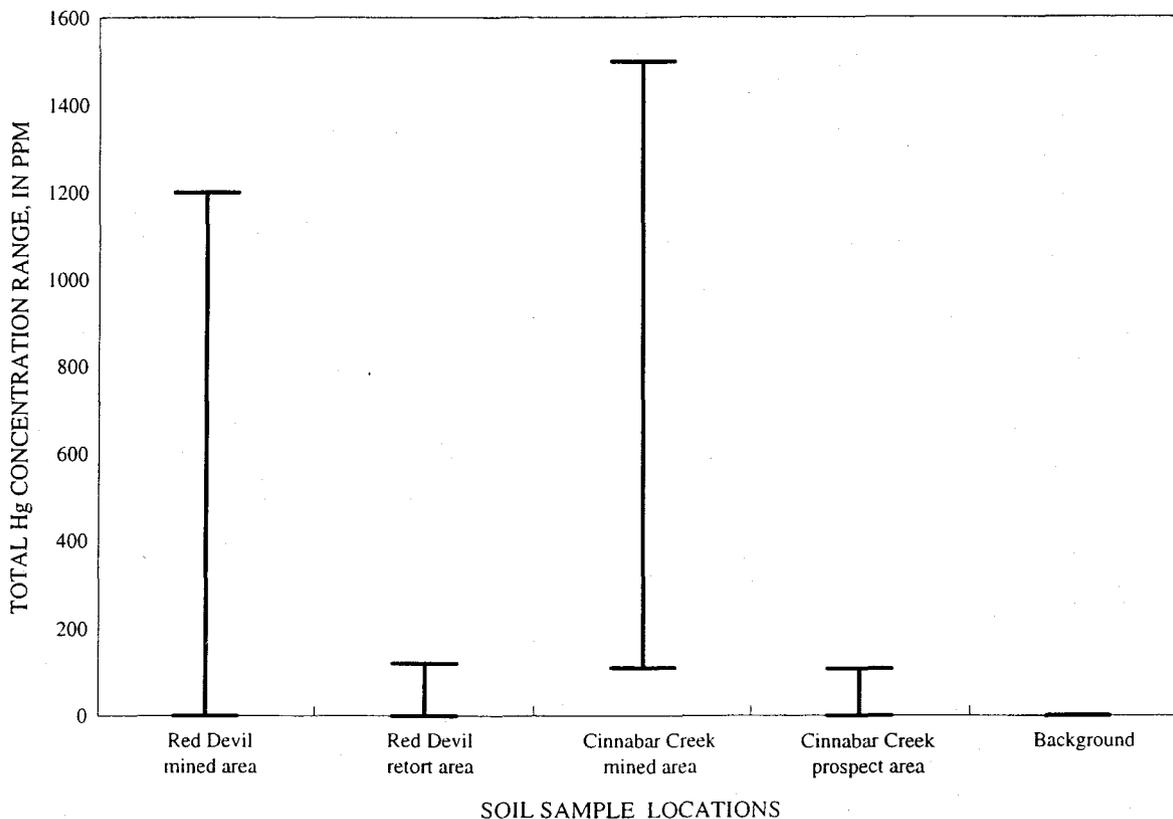


Figure 6. Comparison of total-mercury-concentration ranges (in parts per million) in soils collected from Red Devil and Cinnabar Creek mined areas and unmined areas and regional background sites.

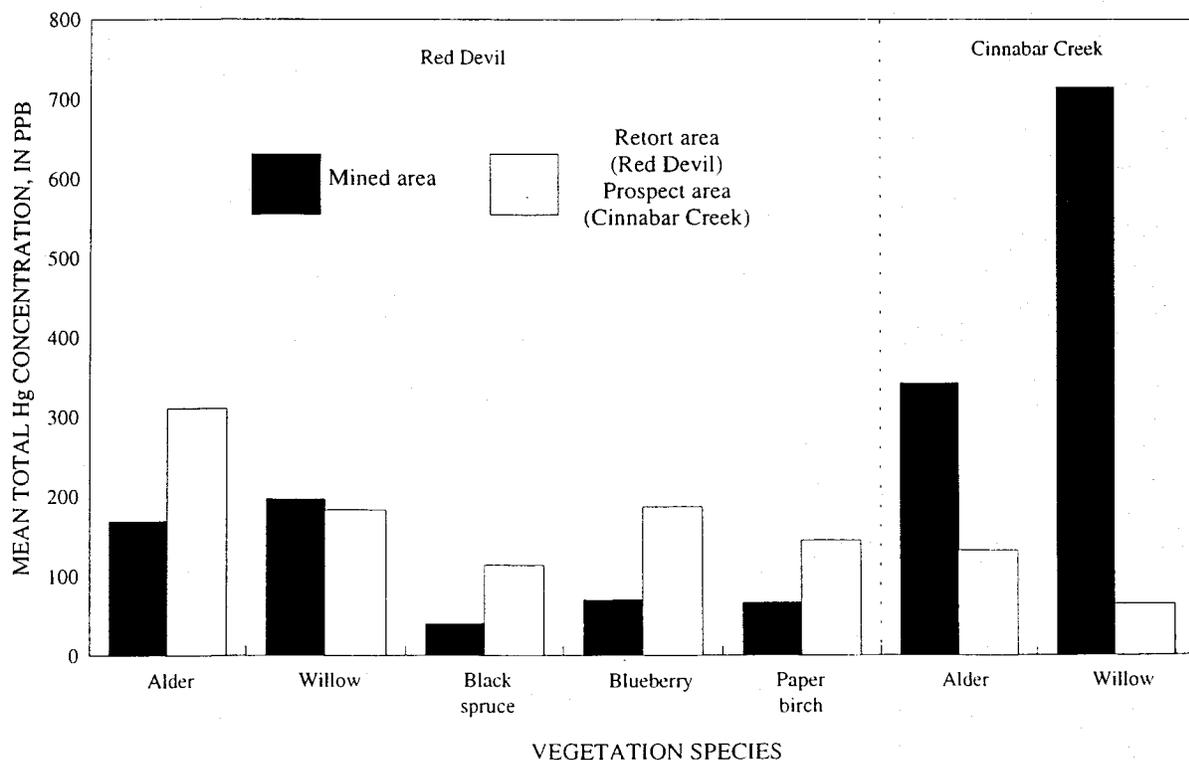
## LIQUID MERCURY VERSUS CINNABAR

At the Red Devil mine, mercury concentrations are higher in the vegetation samples collected from the unmined area where the retort was located than in those samples collected from the mined trench (fig. 7). It is likely that during mining, retort operations released mercury vapor ( $\text{Hg}^0$ ) that later condensed as liquid mercury on the nearby soils. Liquid mercury, owing to its high solubility, is absorbed more readily by plants than is highly insoluble cinnabar (Lodenus, 1994), the most common form of mercury in soil in the mined trench. At the Cinnabar Creek mine, mercury concentrations are much higher in the vegetation samples collected from the mined trench, where liquid Hg has been noted (Gray and others, 1991), than in vegetation collected from a prospect trench where liquid mercury has not been noted and no ore was mined (fig. 7).

Methylmercury concentrations, like total-mercury concentrations, are higher in vegetation samples collected from both mines (0.45 to 36.7 ppb) than in vegetation samples collected from background sites (0.45 and 0.49 ppb). Methylmercury concentrations are generally higher in vegetation samples collected from Cinnabar Creek (0.73 to 36.7 ppb) than in those collected from Red Devil (0.45 to 2.76 ppb) (tables 1, 2). Liquid mercury ( $\text{Hg}^0$ ), a form of mer-

cury more commonly found at Cinnabar Creek mine than at Red Devil mine, is readily converted to the mercuric ( $\text{Hg}^{2+}$ ) ion, which in turn is easily converted to methylmercury. On the other hand, the conversions of mercury in cinnabar ( $\text{HgS}$ ) to methylmercury is slow (McLean and Bledsoe, 1992). Methylmercury levels in vegetation in our study area are generally low—less than 3 percent of total Hg levels—with the exception of sample 042 from the Cinnabar Creek mine, which contains 36.7 percent methylmercury. These data contrast with values from other types of biological tissue collected in southwestern Alaska; Gray and others (1994) reported fish samples in which methylmercury constituted greater than 90 percent of the total mercury content.

Methylmercury concentrations in soils collected from the mined trench at Cinnabar Creek and from the retort area at Red Devil are notably higher than those found at other locations at the mine sites (fig. 8). Liquid mercury is known to be present in the Cinnabar Creek mine trench. Likewise, near the Red Devil retort site, liquid mercury is probably present in the soils from past mining and retorting. In both cases, the presence of liquid mercury most likely explains the elevated methylmercury concentrations found in these soils compared with the levels found in soils collected from backgrounds.



**Figure 7.** Comparison of average total-mercury concentrations (in parts per billion) in leaf-tissue samples from mined areas and unmined areas at Red Devil and Cinnabar Creek mines.

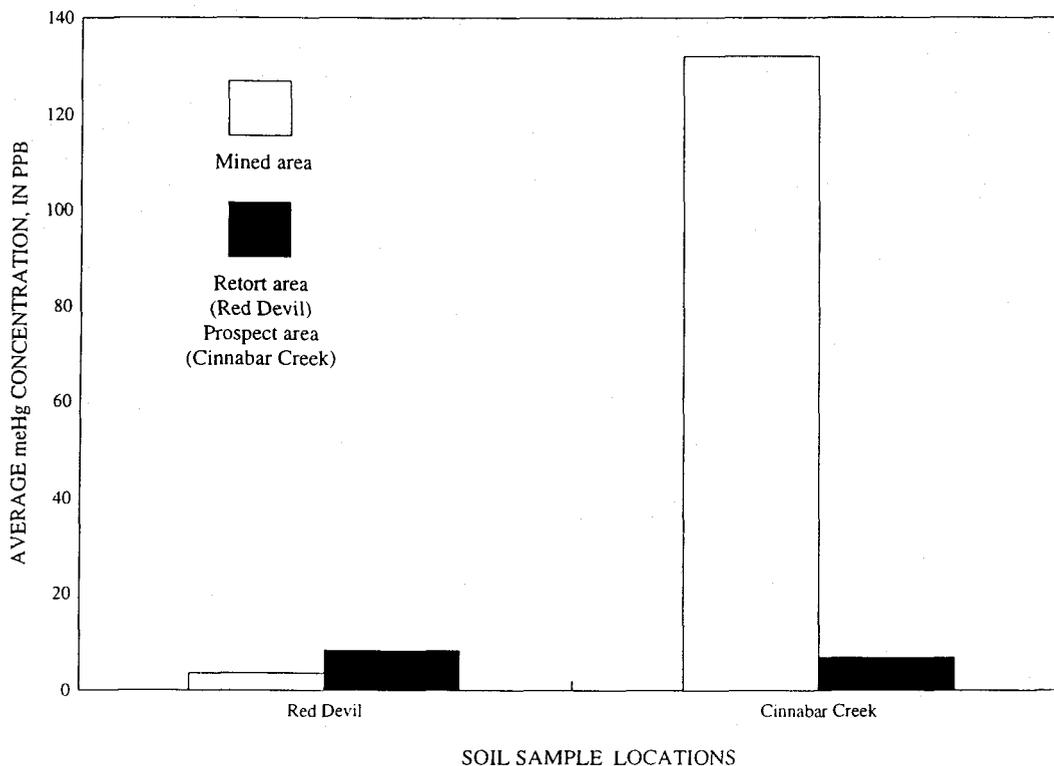
### STREAM-WATER SAMPLES

Some raw unfiltered stream-water samples collected downstream from the Red Devil and Cinnabar Creek mines contain mercury concentrations elevated above background values. Unfiltered stream-water samples collected downstream from the Red Devil mine contain as much as 0.28 ppb Hg, whereas background stream-water samples collected in the region contain less than 0.10 ppb Hg. However, the concentration of mercury in all stream-water samples is below both the 2 ppb drinking-water MCL 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 (Environmental Protection Agency, 1992). In addition, streams at these mines generally are not water supplies for human consumption. Mercury concentrations in the stream-water samples are low, even downstream from the mines, because the primary ore mineral is cinnabar, which is resistant to chemical and physical weathering. The stream-water mercury data indicate that only small amounts of mercury are transported in water, generally as suspended material, because the unfiltered water samples collected downstream from the mines were the only water samples with measurable concentrations of mer-

cury. Furthermore, even when mercury is converted to water-soluble forms and carried in water, it tends to be rapidly sorbed by sediment, including clays, microcrystalline oxides, and organic matter, in the stream environment (Jenne, 1970).

### CONCLUSIONS

Total-mercury and methylmercury concentrations in vegetation samples collected from the Cinnabar Creek and Red Devil mercury mines are elevated relative to regional background samples. We found considerable variation in mercury concentrations between different vegetation species; willow and alder generally contain the highest concentrations of mercury. Elevated mercury concentrations in vegetation are significant because alder twigs are eaten by ptarmigan and willow leaves are an important food for moose (Viereck, 1987). Blueberry, the species most likely to be consumed by residents of the Kuskokwim Mountains region, contains relatively low concentrations of total mercury (30 to 100 ppb in the edible fruit). Methylmercury, the highly toxic form of mercury, is probably not hazardous to humans or wildlife in the region. It generally represents less than 3 percent of the total mercury present in



**Figure 8.** Comparison of average methylmercury concentrations (in parts per billion) in soils collected from Red Devil and Cinnabar Creek mined areas and unmined areas; regional background concentrations are less than 0.1 part per billion.

vegetation samples (although values as high as 36.7 percent occur locally); absolute values of methylmercury concentration are 0.45 to 36.7 ppb. Other studies (Agency for Toxic Substances and Disease Registry, 1994) indicate that chronic exposure (daily for >365 days) to greater than 40 ppm methylmercury is necessary to produce detrimental effects in laboratory animals.

Total mercury and methylmercury concentrations in soil samples collected from the Red Devil and Cinnabar Creek mines are as much as three to four orders of magnitude higher than those in background soil samples collected in this study. However, methylmercury constitutes only a small fraction (<0.2 percent) of the total mercury present in the soil samples. Cinnabar is the most common form of mercury in soils collected from the mines, and the high total-mercury-to-methylmercury ratios in soils indicate low conversion rates of inorganic mercury (cinnabar) to organic mercury (methylmercury) at the mines studied. The low methylmercury concentrations in the soil samples collected in this study suggest that mercury contamination is not a problem at the Cinnabar Creek and Red Devil mines.

All concentrations of mercury in stream-water samples collected in this study are below the 2 ppb drinking-water MCL recommended by the State of Alaska. Stream-water pH in samples collected downstream from the mercury mines are neutral to slightly alkaline and are similar to background values. The dominant ore mineral in the mercury mines is cinnabar, which is highly insoluble in water and resistant to physical and chemical weathering. Therefore, these mines do not easily form acid drainage during weathering. 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 insignificant.

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