

# Spatial Distribution of Chemical Constituents in the Kuskokwim River, Alaska

Water-Resources Investigations Report 99-4177



Cover: Moose swimming in the Kuskokwim River above Stony River, June 1997

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By Bronwen Wang

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## CONVERSION FACTORS AND ABBREVIATED UNITS

	Multiply	by	To obtain
	meter (m)	3.281	foot
	kilometer (km)	0.6214	mile
	square kilometer (km <sup>2</sup> )	0.3861	square mile
	cubic meter per second (m <sup>3</sup> /s)	35.31	cubic foot per second
	metric ton per day	1.02	ton per day

In this report, temperature is reported in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$^{\circ}\text{F} = 1.8 (^{\circ}\text{C}) + 32$$

## OTHER ABBREVIATED UNITS

L, liter

mg/L, milligram per liter

µg/L, microgram per liter

ng/L, nanogram per liter

µm, micrometer

µg/g, microgram per gram

ng/g, nanogram per gram

mg/kg, milligram per kilogram

µS/cm, microsiemen per centimeter at 25 degrees Celsius

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## ABSTRACT

The effects of lithologic changes on the water quality of the Kuskokwim River, Alaska, were evaluated by the U.S. Geological Survey in June 1997. Water, suspended sediments, and bed sediments were sampled from the Kuskokwim River and from three tributaries, the Holitna River, Red Devil Creek, and Crooked Creek. Dissolved boron, chromium, copper, manganese, zinc, aluminum, lithium, barium, iron, antimony, arsenic, mercury, and strontium were detected. Dissolved manganese and iron concentrations were three and four times higher in the Holitna River than in the Kuskokwim River. Finely divided ferruginous materials found in the graywacke and shale units of the Kuskokwim Group are the probable source of the iron. The highest concentrations of dissolved strontium and barium were found at McGrath, and the limestone present in the upper basin was the most probable source of strontium. The total mercury concentrations on the Kuskokwim River decreased downstream from McGrath. Dissolved mercury was 24 to 32 percent of the total concentration. The highest concentrations of total mercury, and of dissolved antimony and arsenic were found in Red Devil Creek. The higher concentrations from Red Devil Creek did not affect the main stem mercury transport because the tributary was small relative to the Kuskokwim River. In Red Devil Creek, total mercury exceeded the concentration at which the U.S. Environmental Protection Agency (USEPA) indicates that

aquatic life is affected and dissolved arsenic exceeded the USEPA's drinking-water standard. Background mercury and antimony concentrations in bed sediments ranged from 0.09 to 0.15 micrograms per gram for mercury and from 1.6 to 2.1 micrograms per gram for antimony. Background arsenic concentrations were greater than 27 micrograms per gram. Sites near the Red Devil mercury mine had mercury and antimony concentrations greater than background concentrations. These concentrations probably reflect the proximity to the ore body and past mining. Crooked Creek had mercury concentrations greater than the background concentration. The transport of suspended sediment-associated trace elements was lower for all elements in the lower river than in the upper river, indicating storage of sediments and their associated metals within the river system.

## INTRODUCTION

### Purpose and Scope

The Kuskokwim River, Alaska, drains a remote basin of about 130,000 km<sup>2</sup> along its 1,130-km course from interior Alaska to the Bering Sea (fig. 1). Although the river basin is largely undeveloped, mercury and placer gold have been mined within the basin (Bundtzen and Miller, 1996). Concerns about the water quality of the river relate primarily to these past mining activities and their continued effects (McBride, 1997). The Kuskokwim River basin



contains placer cinnabar and mined and unmined epithermal mercury ore deposits (Cady and others, 1955; Miller and Bundtzen, 1994). Mercury and associated metal enrichment in the Kuskokwim River could result from both natural processes and human activity. Several studies have focused on the mercury distribution in the Kuskokwim region (Nelson and others, 1977; Gray and others, 1991 and 1994; Bailey and Gray, 1997) and have evaluated both mercury distribution in the smaller drainages of the Kuskokwim basin and the link to plant and animal uptake. The purpose of this study was to focus on the water quality of the Kuskokwim River and selected tributaries by evaluating the chemical composition of the river in relation to lithologic changes.

## Description of Study Area

The upper Kuskokwim River is bordered by the Alaska Range to the southeast and by the Kuskokwim Mountains to the northwest (fig. 1). Upstream from McGrath, the North, South, and East Forks, and a host of smaller tributaries, combine to form the Kuskokwim River. From McGrath to its confluence with the Holitna River, the Kuskokwim flows slowly along the base of the Kuskokwim Mountains. Near Sleetmute, the Holitna River joins the Kuskokwim from the south. The river then swings northward bisecting the Kuskokwim Mountains where it narrows and becomes more channelized. The river flows past the historic Red Devil mercury mine and at Crooked Creek, swings southward and westward exiting the Kuskokwim Mountains at Aniak. The river then broadens and the main channel becomes less defined as it crosses the Kuskokwim delta.

The upper river drains primarily lower Paleozoic rocks of Cambrian through Devonian age (fig. 1). The sedimentary rocks include limestone, dolostone, argillite, chert, and

graywacke (Beikman, 1980). The mid-river reach drains the Upper Cretaceous Kuskokwim Group, a regionally extensive basin-fill sedimentary sequence. This sequence is dominantly deep marine turbidites with shallow-marine and fluvial strata that were deposited along the basin margins (Miller and Bundtzen, 1994). The Kuskokwim Group constitutes the principal rocks of the Kuskokwim Mountains and consists of interbedded graywacke and shale (Miller and Bundtzen, 1994; Cady and others, 1955). Most of the known cinnabar and stibnite deposits occur within the Kuskokwim Group (Sainsbury and MacKevett, 1965). The Red Devil mercury mine is one such deposit. Along with cinnabar and stibnite, the Red Devil deposit contains minor amounts of realgar, orpiment, pyrite, and hematite (MacKevett and Berg, 1963). These deposits and the mining of them could contribute elements such as mercury, antimony, or arsenic to the river system. The lower river drains Quaternary alluvial and glacial deposits (fig. 1).

## METHODS

Water, suspended-sediment, and bed-sediment samples were collected and water discharge was measured in June 1997 along the Kuskokwim River from McGrath to Akiak (fig. 1, table 1). In addition, three tributaries—the Holitna River, Red Devil Creek, and Crooked Creek—were also sampled (table 1). The sites were sampled using a lagrangian sampling design (Meade and Stevens, 1990). In this design, sites are sampled in downstream sequence, and, ideally, the same mass of water downriver is sampled. This allows changes occurring within the water mass to be identified. The sites were selected to bracket both the major lithologic changes and the mining regions of the Kuskokwim River.

**Table 1.** Sampling sites for Kuskokwim River and tributaries[km<sup>2</sup>, square kilometer; km, kilometer; --, not available or not applicable]

Site No. (fig. 1)	USGS station name	USGS station number	Drainage basin area (km <sup>2</sup> )	Distance from Bethel (km)	Remarks
<b>Kuskokwim River Main Stem</b>					
KR1	Kuskokwim River at McGrath	15303600	11,700	670	Upper river above the Kuskokwim Group
KR2	Kuskokwim River above Stony River	614633156334300	18,900	450	Within the Kuskokwim Group, but above the historic Red Devil mercury mine
KR3	Kuskokwim River above Holitna River	614031157074000	27,400	400	Within the Kuskokwim Group, but above the historic Red Devil mercury mine
KR4A	<sup>a</sup> Kuskokwim River above site KR4	--	--	--	Bed-sediment sampling site only. Upstream from site KR4 and about 0.4 kilometer down- stream from site T2
KR4	Kuskokwim River below Red Devil Mine	614722157201900	29,400	383	Within the Kuskokwim Group, below the his- toric Red Devil mercury mine and the conflu- ence with the Holitna River
KR5	Kuskokwim River at Crooked Creek	15304000	31,100	327	Within the Kuskokwim Group, below the his- toric Red Devil mercury mine and the conflu- ence with the Holitna River
KR6	Kuskokwim River above Aniak River	613551159263200	34,300	217	Within the alluvial and glacial deposits
KR7	Kuskokwim River near Akiak	605329161144900	--	61	Within the alluvial and glacial deposits
<b>Kuskokwim River Tributaries</b>					
T1	Holitna River near Sleetmute	614040157095000	6,430	396	Major tributary to the Kuskokwim River. Originates in shale-rich portion of the Kuskokwim Group, with a Paleozoic lime- stone cross cutting the middle course of the river (Cady and others, 1955).
T2	Red Devil Creek near Red Devil	614544157183400	--	386	Small drainage draining the historic Red Devil mine site that discharges directly into the Kuskokwim River.
T3	Crooked Creek at Crooked Creek	615218158072500	--	323	Small tributary to the Kuskokwim River. In early part of the 1900's, placer deposits were mined in the upper tributaries to Crooked Creek. In addition to gold, these deposits con- tain placer cinnabar. Drainage is also site of current prospecting lode gold (Dodd, 1996).

<sup>a</sup>Not official USGS station

## Discharge

Discharge was measured using a standard AA meter, except at Red Devil Creek where flow was estimated by timed drift. Discharge measurements (table 2) were made the week before water-quality sample collection for the Kuskokwim River between Stony River and Crooked Creek (sites KR2 to KR5) and the Holitna River (site T1). Temporary stage gages were used to determine stage changes that occurred before water-quality sampling. Discharge at these sites was corrected for stage change by correlating the discharge at these sites to the continuous discharge record at Crooked Creek (KR5). Discharge measurements (table 2) were made just before sample collection for the remaining three sites on the Kuskokwim River (sites KR1, KR6, and KR7), and the two other tributaries (sites T2 and T3).

## Water Sample Collection

Vertically integrated samples collected from the centroid of five equal discharge increments (EDI) were combined into depth- and width-integrated water samples (Edward and Glysson, 1988). The five EDI points were calculated from the measured discharge. Depth- and width-integrated water samples were collected at all river sites using a D-77 sampler (Edwards and Glysson, 1988) equipped with a Teflon head and a 3-L Teflon bottle. When river depth exceeded 4.5 m (the isokinetic depth limit for the rigid bottle), a 3-L Teflon bag was used in place of the bottle. The two small drainages, Crooked Creek and Red Devil Creek, were sampled by wading. A depth- and width-integrated sample was collected from Crooked Creek using a DH-81. Verticals were combined in a compositing churn at these site. At Red

**Table 2.** Drainage basin area, water discharge, suspended-sediment concentration, and percent suspended sediment <62 micrometers for the Kuskokwim River, Holitna River, Red Devil Creek, and Crooked Creek, June 1997

[km<sup>2</sup>, square kilometer; m<sup>3</sup>/s, cubic meter per second; mg/L, milligram per liter; --, not available]

Site	Drainage basin area (km <sup>2</sup> )	Water discharge (m <sup>3</sup> /s)	Suspended sediment	
			Concentration (mg/L)	Percent <62 micrometers
<b>Kuskokwim River</b>				
KR1	11,700	413	353	81
KR2	18,900	569	113	83
KR3	27,400	776	195	67
KR4	29,400	1,102	64	66
KR5	31,100	1,141	67	82
KR6	34,300	1,365	55	85
KR7	--	1,623	60	82
<b>Tributaries</b>				
T1	6,430	314	13	93
T2	--	0.02 <sup>a</sup>	--	--
T3	--	7.34	31	96

<sup>a</sup>Estimated

Devil Creek, a composite dip sample consisting of dips from five points across the stream was taken. Specific conductance, dissolved oxygen, pH, and temperature were measured across the cross section using a calibrated Hydrolab at all sites except at Red Devil Creek, where they were taken from the dip sample.

Samples for major ion and trace element chemistry, and nutrients were processed according to methods described by Horowitz and others (1994). Major ion, trace element, and nutrient samples were filtered through a 0.45- $\mu\text{m}$  capsule filter. Dissolved organic carbon samples were filtered through a 0.45- $\mu\text{m}$  silver filter; the filter was retained for suspended organic carbon analysis. Trace-element samples were preserved with nitric acid, and nutrient samples were chilled. The filtered samples will be referred to as “dissolved concentrations.”

Separate samples were taken for mercury and methyl mercury analyses. Samples were collected to a 1-m depth at the five EDI points. Depth integration could not be done for these samples because a large Teflon compositing container was not available. However, a five-point width integration across the river was collected because incomplete horizontal mixing was suspected at some sites. Total mercury and total methyl mercury samples, which were collected at all sites, were not filtered. Unfiltered samples will be referred to as “total concentrations.” At sites KR3 and KR5, both total and dissolved samples were collected for the mercury and methyl mercury analyses. All equipment and sample bottles used for mercury and methyl mercury sampling were boiled in 50 percent nitric acid before being sent to the field. Total mercury was preserved with 10 percent HCl and methyl mercury samples were frozen.

## **Suspended-Sediment Sample Collection**

Suspended-sediment concentration samples were collected using the method of Meade and Stevens (1990). At each EDI point, a vertically integrated sample was collected for suspended-sediment concentration. The vertical was passed through a 62- $\mu\text{m}$  sieve into a graduated cylinder, the volume was recorded, and the samples were poured into a sediment churn for compositing. The <62- $\mu\text{m}$  sample was taken from the churn and the sieve was rinsed into a sediment jar for the >62- $\mu\text{m}$  sample. Total sediment concentration was calculated as the sum of these two fractions.

Suspended-sediment samples for chemical analyses were collected from five of the seven Kuskokwim River sites: Kuskokwim River at McGrath (site KR1), above the Holitna River (site KR3), below Red Devil Mine (site KR4), at Crooked Creek (site KR6), and above Aniak (site KR7). Unfiltered water samples for sediment-associated trace elements were stored in 5-gallon polyethylene carboys and shipped to the USGS laboratory where they were centrifuged, freeze dried, and sieved through a 62- $\mu\text{m}$  sieve. Samples will be referred to as “suspended-sediment-associated trace elements.”

## **Bed-Sediment Sample Collection**

Low water facilitated locating depositional zones for bed-sediment collection. Composites of the fine sediments were collected by combining samples from multiple points into glass bowls (Shelton and Capel, 1994). Samples were kept at 4 °C until they were processed in the laboratory. In the laboratory, samples were freeze dried and dry sieved through a 62- $\mu\text{m}$  nylon mesh sieve. Both the <62- $\mu\text{m}$  and the >62- $\mu\text{m}$  fractions were analyzed. Samples of bed sediment were taken near all surface-water sites except at KR4. A separate site was established for bed-sediment sampling on the

Kuskokwim River below the Red Devil Mine (site KR4A). This site is upstream from site KR4 and about 0.4 km below Red Devil Creek (site T2). Red Devil Mine operated on the left bank of the Kuskokwim River, and other mercury deposits are mapped near the river's left bank (Miller and Bundtzen, 1994). At sites KR4A and KR5, samples were collected from both the right and left banks of the Kuskokwim River to determine if a compositional difference between banks could be detected.

### Quality-Control Samples

A duplicate filtered water sample and an aqueous field blank were collected at site KR2. Duplicate samples for total mercury and total methyl mercury were collected at site KR7. Duplicate bed-sediment samples were taken at all sites except KR6, where only a single composite sample was obtained.

Detection limits and methods for the inorganic element and nutrient analyses are given in table 3 (Patton and Truitt, 1992; Faires, 1993; Fishman, 1993; Horvat and others, 1993; U.S. Environmental Protection Agency, 1995; Struzeski and others, 1996). Suspended-sediment and bed sediment samples were digested using a combination of hydrofluoric acid and perchloric acid prior to analyses (A.J. Horowitz, USGS, oral commun., 1999).

### Data Analysis

Sediment and trace-element transport was calculated using the instantaneous discharge at a given site and the corresponding sediment and trace-element concentration. Prior to calculating sediment-associated trace-element transport, the weight-based concentration was converted from a volume-based concentration by:

$$[C_{\text{ssate}}, \text{ in } \mu\text{g/L}] = [C_{\text{ssate}}, \text{ in } \mu\text{g/g}] \times [C_{\text{ss}}, \text{ in mg/L}] \times 10^{-3}$$

where  $C_{\text{ssate}}$  is the concentration of the suspended-sediment-associated trace element and  $C_{\text{ss}}$  is the suspended-sediment concentration. The transport was then converted to a daily value. This conversion assumes that the instantaneous discharge, the sediment concentration, and the trace-element concentration are representative of the daily time step. This is a reasonable assumption when the stage is not rapidly changing.

The USGS has collected water-quality data at the Kuskokwim River at Crooked Creek (site KR5) since 1951. Data collected during the 1997 sampling were compared to historical values. Comparisons between dissolved constituents collected in 1997 and those from the historical record can be made directly. Historically, unfiltered samples were taken as a measure of the total constituent concentration. In 1997, this type of sample was not collected, but rather the suspended sediment was analyzed directly for trace elements. To compare the 1997 sampling concentrations to the historical total trace-element concentrations, the suspended-sediment-associated trace-element concentrations were converted to a volume-based concentration and added to the measured dissolved concentration. The final calculated total is given by:

$$[C_{\text{total}}, \text{ in } \mu\text{g/L}] = [C_{\text{ssate}}, \text{ in } \mu\text{g/L}] + [C_{\text{dissolved}}, \text{ in } \mu\text{g/L}].$$

Probability plots were used in defining mercury, antimony and arsenic background concentrations in the Kuskokwim River basin bed sediments. Probability plots were constructed by plotting the concentration of the element of interest against quantiles of a standard normal distribution. If the data fit a single normal distribution, the resulting plot will be a straight line (Velz, 1984). Nonlinearity in probability plots indicates that the data do not fit a normal distribution. Outlying data will appear as a departure from the trend of the rest of the data (Helsel and Hirsch, 1992). If the data con-

**Table 3. Reporting limits for chemical analysis of water samples and sediment samples**

[mg/L, milligram per liter; µg/L, microgram per liter; ng/L, nanogram per liter; µg/g, microgram per gram; %, percent; --, not applicable]

Methods: ICP, inductively coupled plasma  
 FAA, flame atomic absorption  
 HGAA, hydride generation atomic absorption  
 ASF, automated-segmented flow

IC, ion-exchange chromatography  
 ISE, ion selective electrode  
 ICP-MS, inductively coupled plasma—mass spectrometry  
 CVAFS, cold vapor atomic fluorescence spectrometry

Constituent	Method of analysis	Water		Sediment	
		Reporting limit	Unit	Reporting limit	Unit <sup>a</sup>
Calcium	ICP	0.02	mg/L as Ca	--	--
Magnesium	ICP	0.004	mg/L as Mg	--	--
Sodium	ICP	0.1	mg/L as Na	--	--
Potassium	FAA	0.1	mg/L as K	--	--
Sulfate	IC	0.1	mg/L as SO <sub>4</sub>	--	--
Chloride	IC	0.1	mg/L as Cl	--	--
Fluoride	ISE	0.1	mg/L as F	--	--
Silica	ICP	0.1	mg/L as SO <sub>2</sub>	--	--
Boron	ICP	4	mg/L as B	--	--
Arsenic	HGAA	1	µg/L as As	0.1	µg/g as As
Iron	ICP	10	µg/L as Fe	0.1	% as Fe
Lithium	ICP	4	µg/L as Li	1	µg/g as Li
Strontium	ICP	1	µg/L as Sr	1	µg/g as Sr
Antimony	ICP-MS	1	µg/L as Sb	0.1	µg/g as Sb
Copper	ICP-MS	1	µg/L as Cu	1	µg/g as Cu
Molybdenum	ICP-MS	1	µg/L as Mo	5	µg/g as Mo
Manganese	ICP-MS	1	µg/L as Mn	10	µg/g as Mn
Chromium	ICP-MS	1	µg/L as Cr	1	µg/g as Cr
Aluminum	ICP-MS	1	µg/L as Al	0.1	µg/g as Al
Zinc	ICP-MS	1	µg/L as Zn	1	µg/g as Zn
Barium	ICP-MS	1	µg/L as Ba	1	µg/g as Ba
Mercury	CVAFS	0.04	ng/L as Hg	0.01	µg/g as Hg
Methyl mercury	CVAFS	0.02	ng/L as Hg	0.02	µg/g as Hg
Titanium	--	--	--	0.01	% as Ti
Phosphorus	--	--	--	0.01	% as P
Total carbon	--	--	--	0.1	% as C
Total sulfur	--	--	--	0.1	% as S
Nitrite	Colorimetry ASF cadmium reduction	0.001	mg/L as N	--	--
Nitrate + nitrite	Diazonation ASF microkjeldahl	0.005	mg/L as N	--	--
Total phosphorus <sup>b</sup>	Digestion, color	0.01	mg/L as P	0.01	% as P
Dissolved organic carbon	Dohrmann	0.1	mg/L as C	--	--
Suspended organic carbon	Dohrmann	0.1	mg/L as C	--	--

<sup>a</sup>Dry weight basis<sup>b</sup>Unfiltered sample

tain outliers, the concentration at the first break point has been used as background concentrations in bed sediments (Velz, 1984; Deacon and Stephens, 1998). For the probability plots constructed, the plotting position was calculated using the Cunnane formulation as described by Helsel and Hirsch (1992). All bed-sediment data were used to determine the plotting position of the samples, but one sample from site T2 was not plotted so that the shape of the plot at low concentrations could be evaluated.

## QUALITY CONTROL

The protocols used in this study were designed to reduce the potential for trace-element contamination of the sample, allowing trace-metal concentrations to be determined in the microgram per liter concentration range (Horowitz and others, 1994). Analyses of the aqueous field blanks collected indicated that the procedures followed were capable of providing trace-element data in this range. The only trace element detected in a blank analysis was copper at 0.23  $\mu\text{g/L}$  (table 4). Consequently, as much as 15 percent of the copper detected could have been from contamination. In addition, copper concentrations in duplicate samples differed by 0.4  $\mu\text{g/L}$ . The measured copper values ranged from <1 to 2.7  $\mu\text{g/L}$  and are not significantly different. Calcium, magnesium, and silica were also detected in the blanks (table 4), but at concentrations several orders of magnitude lower than those reported in the environmental sample. Agreement between duplicate water samples was generally good. However, zinc concentrations between duplicates was <1 and 2.7  $\mu\text{g/L}$ . Detected concentrations for zinc ranged from 1.3 to 3.2  $\mu\text{g/L}$  and, like copper, are not significantly different. No further analysis of aqueous copper or zinc in the system was done.

Comparisons were made between data collected in 1997 and the historical data from

the Kuskokwim River at Crooked Creek (site KR5). The specific conductance value of 194  $\mu\text{S/cm}$  for the 1997 sampling (table 4) was greater than the 75<sup>th</sup> percentile for the historical data for the open-water period (table 5). The major ion concentrations were near their respective inner quartile range for the historical record: calcium was at the median, magnesium was near the median, alkalinity was below the median and above the 25<sup>th</sup> percentile, and sulfate was slightly greater than the 75<sup>th</sup> percentile. Dissolved barium and strontium fell within the inner quartile range, but dissolved iron and manganese fell below. The calculated totals for iron (2,944  $\mu\text{g/L}$ ), arsenic (<3  $\mu\text{g/L}$ , 2.5 based on  $C_{\text{ssate}}$  alone), and manganese (76  $\mu\text{g/L}$ ) concentrations are below the inner 25<sup>th</sup> percentile of the historical values for the open-water season (table 5). The manganese concentration was near the 25<sup>th</sup> percentile and this could be accounted for by the difference between direct measurement and calculation. Iron and arsenic are 16 and 25 percent lower than their respective 25<sup>th</sup> percentiles.

In 1997, unusually low water predominated throughout the year (Benson and others, 1998). Cool weather in May delayed the onset of glacier melt resulting in both low June flows and low sediment concentrations. The historical mean discharge at site KR5 for June is 2,338  $\text{m}^3/\text{s}$ . In 1997, the mean discharge for June was 1,165  $\text{m}^3/\text{s}$ , about half the mean discharge for the period of record and only about 200  $\text{m}^3/\text{s}$  above the historical minimum (Benson and others, 1998). One consequence of the lower flow was low sediment concentrations. The historical median sediment concentration during open water is 133.5  $\text{mg/L}$  with an inner quartile range from 87 to 223  $\text{mg/L}$  (table 5). During June 1997, the sediment concentration was measured at 67  $\text{mg/L}$ , which is lower than the 25<sup>th</sup> percentile of the period of record. The suspended-sediment concentration was 23 percent lower than the historical 25<sup>th</sup> percentile. The low sediment concentration can account for the

**Table 4.** Field measurements, and major and trace ions, nutrients, and dissolved and suspended organic carbon detected in the Kuskokwim River and its tributaries [mg/L, milligram per liter; µg/L, microgram per liter; µS/cm, microsiemen per centimeter; °C, degree Celsius; <, actual value is less than value shown; --, no data]

Property or constituent	Unit	Kuskokwim River								Tributaries			Blank
		KR1	KR2	KR2 Duplicate	KR3	KR4	KR5	KR6	KR7	T1	T2	T3	
Specific conductance	µS/cm	319	253	253	214	194	194	191	178	93	176	131	--
pH		8.2	8	8	7.7	7.4	8.2	7.8	8.1	7.6	7.8	7.9	--
Alkalinity, dissolved	mg/L as CaCO <sub>3</sub>	106	96	97	73	73	65	64	64	37	72	52	--
Calcium, dissolved	mg/L as Ca	43	38	38	31	27	25	24	23	11	17	14	0.008
Magnesium, dissolved	mg/L as Mg	12	9.1	9.2	7.4	6.4	6	5.9	5.5	3	11	4.9	0.001
Sodium, dissolved	mg/L as Na	2.4	2.2	2.2	2	2.1	2	2	2.1	2	2.8	3.4	<0.025
Potassium, dissolved	mg/L as K	1.1	1	0.98	0.96	0.81	0.79	2.6	0.7	0.36	0.41	0.39	--
Sulfate, dissolved	mg/L as SO <sub>4</sub>	56	38	38	30	23	23	22	20	6.2	13	4.8	--
Chloride, dissolved	mg/L as Cl	0.39	0.54	0.46	0.52	0.5	0.44	0.37	0.51	0.55	0.34	1.9	--
Fluoride, dissolved	mg/L as F	0.18	0.19	0.2	0.2	0.2	0.18	0.17	0.16	<0.10	0.1	<0.10	--
Silica, dissolved	mg/L as SO <sub>2</sub>	7.4	7.3	7.3	6.9	6.8	6.6	6.5	6.3	7.4	6.6	7.3	0.038
Bicarbonate, dissolved <sup>a</sup>	mg/L as HCO <sub>3</sub>	129	117	118	89	89	79	78	78	45	88	63	--
Boron, dissolved	µg/L as B	7.8	7.1	7.9	6.5	7.7	4.9	6.3	--	5	9.1	9.5	<2
Arsenic, dissolved	µg/L as As	1	1	1	1	1	<1	1	1	1	180	1	<2
Iron, dissolved	µg/L as Fe	40	54	59	84	120	130	100	84	410	31	510	<3
Lithium, dissolved	µg/L as Li	4	5	5	5	<4	<4	<4	<4	<4	5	<4	--
Strontium, dissolved	µg/L as Sr	296	231	232	188	162	152	149	137	59	83	112	<0.10
Antimony, dissolved	µg/L as Sb	<1	<1	<1	<1	<1	<1	<1	<1	<1	281	<1	<0.20
Copper, dissolved	µg/L as Cu	2.7	1.5	1.9	2.3	1.5	<1	1.1	1.6	<1	1.4	1.4	0.23
Molybdenum, dissolved	µg/L as Mo	1.6	1.2	1.1	1.2	<1	1	1	<1.0	<1	<1.0	<1.0	<0.20
Manganese, dissolved	µg/L as Mn	3.5	3.3	3.5	3.5	3.5	2.5	2.7	3.4	15	17	47	<0.10
Chromium, dissolved	µg/L as Cr	1.9	1.6	1.6	<1	1	1.2	1.1	1.1	<1	1.6	<1.0	<0.20
Aluminum, dissolved	µg/L as Al	18	10	11	13	16	12	14	10	5.4	4.7	25	<0.30
Zinc, dissolved	µg/L as Zn	<1	<1	2.7	<1	2.3	1.5	3.2	<1	1.3	<1.0	1.7	<0.50
Barium, dissolved	µg/L as Ba	63	52	52	43	36	35	35	30	16	30	47	<0.20
Nitrite, dissolved	mg/L as N	0.002	0.003	0.003	0.003	--	0.002	0.002	0.001	0.003	0.003	0.003	--
Nitrate + nitrite, dissolved	mg/L as N	0.081	0.081	0.082	0.067	--	0.042	0.024	0.007	0.015	0.106	0.089	--
Total phosphorus <sup>b</sup>	mg/L as P	0.23	0.015	0.052	0.044	--	<0.010	0.02	<0.010	<0.010	0.064	<0.010	--
Dissolved organic carbon	mg/L as C	2.0	2.4	2.4	2.4	--	2.3	2.2	2.4	1.8	--	6.8	--
Suspended organic carbon	mg/L as C	1.8	1	0.6	0.2	--	0.9	1	1	0.2	--	0.8	--

<sup>a</sup>Calculated from alkalinity<sup>b</sup>Unfiltered sample

**Table 5.** Historical chemical analysis during the open-water period (mid-May to mid-October) for the Kuskokwim River at Crooked Creek

[mg/g, milligram per gram; mg/L, milligram per liter; µg/L, microgram per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

Property or constituent	Unit	Period of record	Mean	Median	<sup>a</sup> Q <sub>1</sub>	<sup>b</sup> Q <sub>3</sub>	Reporting limit
Suspended sediment	mg/g	1967-97	188	134	87	223	1.0
Specific conductance	µS/cm	1951-98	171	176	152	193	1.0
pH		1951-98	7.6	7.6	7.3	7.8	0.1
Dissolved oxygen	mg/L	1975-97	10.6	10.3	9.9	11.25	0.1
Alkalinity	mg/L as CaCO <sub>3</sub>	1951-97	70	73	64	80	1.0
Calcium	mg/L as Ca	1951-96	24.6	25	21	28	0.1
Magnesium	mg/L as Mg	1951-96	5.6	5.5	4.6	6.4	0.1
Sulfate	mg/L as SO <sub>4</sub>	1951-96	16.7	17	13	20	0.1
Silica	mg/L as SiO <sub>2</sub>	1951-96	8.3	8	7.1	9.45	0.1
Arsenic, total	µg/L as As	1975-82	4.4	4	3	5	1
Barium, dissolved	µg/L as Ba	1980-96	35.9	35	30	41	1
Iron, total	µg/L as Fe	1975-82	5438	4500	3700	7300	10
Iron, dissolved	µg/L as Fe	1975-96	227	225	140	300	10
Manganese, total	µg/L as Mn	1975-82	130	130	80	170	10
Manganese, dissolved	µg/L as Mn	1975-96	12.2	6.5	5	9	4
Strontium, dissolved	µg/L as Sr	1975-96	130	140	99	160	10

<sup>a</sup>25<sup>th</sup> percentile  
<sup>b</sup>75<sup>th</sup> percentile

low total iron, arsenic, and manganese concentrations, because the suspended-sediment concentration is required for the calculated 1997 totals. The concentrations detected in 1997 probably reflect a greater baseflow contribution than is normally present during open water. A greater percentage of baseflow would be consistent with the higher specific conductance, magnesium, and strontium concentrations, as well as the lower sediment, total iron, total manganese, and total arsenic concentrations. With the exception of dissolved manganese, all concentrations fell within the inner quartile

range when the entire population of historical measurements is considered.

Generally, good agreement between duplicate bed-sediment samples was found (sets A and B, table 6). Exceptions were at site KR2 where mercury concentration differed twentyfold and at site T2 (Red Devil Creek) where duplicate samples had mercury, arsenic, antimony, and manganese concentrations that varied over several orders of magnitude (table 6). (Note: See the “*Bed Sediment*” section later in this report for an explanation of the Canadian ISQG and PEL cited on table 6.)

**Table 6.** Chemical analysis for bed sediments from the Kuskokwim River, Holitna River, Red Devil Creek, and Crooked Creek  
 [µm, micrometer; µg/g, microgram per gram; %, percent; <, less than actual value shown; microgram per gram given in dry weight basis; footnotes at end of table]

Site	Sieve fraction Bulk/<62 µm	% <62 µm	Silver µg/g	Copper µg/g	Lead µg/g	Zinc µg/g	Cadmium µg/g	Chromium µg/g	Cobalt µg/g	Nickel µg/g	Barium µg/g	Vanadium µg/g	Lithium µg/g	Beryllium µg/g
<b>Kuskokwim River</b>														
KR1														
Set A	Bulk		<0.5	21	13	81	0.5	<sup>a</sup> 55	10	33	1000	93	34	1.8
Set A	<62µm	16	<0.5	32	13	91	0.6	76	13	38	1000	110	33	1.7
Set B	Bulk		<0.5	19	11	77	0.3	<sup>a</sup> 55	9	30	970	92	31	1.6
Set B	<62µm	15	<0.5	49	10	92	0.5	78	12	38	980	110	32	1.7
KR2														
Set A	Bulk		<0.5	26	13	96	0.4	<sup>a</sup> 64	11	35	950	100	35	1.7
Set A	<62µm	37	<0.5	32	12	94	0.4	79	13	40	940	110	37	1.7
Set B	Bulk		<0.5	29	16	100	0.8	<sup>a</sup> 69	12	38	1000	110	40	1.7
Set B	<62µm	36	<0.5	35	17	100	0.7	81	13	41	980	120	40	1.8
KR3														
Set A	Bulk		<0.5	31	15	110	0.7	<sup>a</sup> 70	12	37	1000	110	43	1.8
Set A	<62µm	46	<0.5	34	15	100	0.7	78	13	40	1000	120	39	1.8
Set B	Bulk		<0.5	32	14	110	0.5	<sup>a</sup> 70	12	38	1000	110	42	1.8
Set B	<62µm	47	<0.5	35	17	100	0.7	78	14	40	1000	120	41	1.8
KR4A Left bank														
Set A	Bulk		<0.5	18	12	77	0.3	<sup>a</sup> 57	10	29	900	92	35	1.5
Set A	<62µm	22	<0.5	25	12	82	0.3	76	12	35	860	110	36	1.6
Set B	Bulk		<0.5	18	11	82	0.3	<sup>a</sup> 60	10	30	890	95	37	1.6
Set B	<62µm	22	<0.5	23	13	79	0.3	76	12	34	850	110	35	1.5
KR4A Right bank														
Set A	Bulk		<0.5	19	13	83	0.4	<sup>a</sup> 60	10	30	970	94	35	1.9
Set A	<62µm	15	<0.5	30	11	95	0.5	78	13	38	960	120	38	1.8
Set B	Bulk		<0.5	21	13	87	0.4	<sup>a</sup> 60	10	31	970	95	35	1.8
Set B	<62µm	21	<0.5	30	12	93	0.5	78	13	37	960	110	38	1.8
KR5 Right bank														
Set A	Bulk		<0.5	22	15	88	0.3	<sup>a</sup> 59	11	32	980	95	39	1.6
Set A	<62µm	30	<0.5	32	14	100	0.6	79	14	40	960	120	40	1.6
Set B	Bulk		<0.5	22	13	88	0.5	<sup>a</sup> 59	11	32	1000	95	39	1.6
Set B	<62µm	29	<0.5	31	13	96	0.7	79	14	40	960	120	39	1.6
KR 5 Left bank														
Set A	Bulk		<0.5	20	12	85	0.4	<sup>a</sup> 59	10	30	950	92	37	1.8
Set A	<62µm	19	<0.5	24	14	81	0.4	75	12	34	890	110	34	1.8
Set B	Bulk		<0.5	18	13	85	0.4	<sup>a</sup> 58	10	30	950	92	36	1.7
Set B	<62µm	21	<0.5	25	13	82	0.4	73	11	34	910	110	35	1.8
KR6														
Set A	Bulk		<0.5	21	13	90	0.4	<sup>a</sup> 62	11	32	960	97	38	1.7
Set A	<62µm	26	<0.5	27	14	88	0.5	75	13	37	910	110	38	1.7
KR7														
Set A	Bulk		<0.5	28	12	110	0.5	<sup>a</sup> 68	13	38	1000	110	41	1.8
Set A	<62µm	59	<0.5	36	17	110	0.6	81	14	43	1000	120	45	1.8
Set B	Bulk		<0.5	28	13	110	0.5	<sup>a</sup> 68	13	38	990	110	43	1.8
Set B	<62µm		<0.5	35	16	110	0.6	80	14	42	990	120	44	1.7
<b>Tributaries</b>														
T1 (Holitna River)														
Set A	Bulk		<0.5	14	10	69	0.3	<sup>a</sup> 56	10	28	870	93	33	1.2
Set A	<62µm	22	<0.5	23	9	77	0.4	75	13	35	780	110	36	1.2
Set B	Bulk		<0.5	17	9	80	0.3	<sup>a</sup> 63	11	31	820	100	35	1.2
Set B	<62µm	30	<0.5	18	10	68	0.3	72	12	32	730	110	32	1.2
T2 (Red Devil Creek)														
Set A	Bulk		<0.5	17	10	76	0.2	<sup>a</sup> 57	10	29	900	90	33	1.8
Set A	<62µm	21	<0.5	36	12	85	0.4	76	12	35	860	110	36	1.6
Set B	Bulk		<0.5	61	19	120	0.5	<sup>b</sup> 140	33	88	1200	140	110	1.5
Set B	<62µm	16	<0.5	81	21	130	0.6	98	40	99	1100	120	66	1.4
T3 (Crooked Creek)														
Set A	Bulk		<0.5	20	11	100	0.4	<sup>a</sup> 71	15	34	850	110	37	1.3
Set A	<62µm	36	<0.5	20	14	81	0.3	75	15	33	860	110	36	1.3
Set B	Bulk		<0.5	25	16	100	0.3	<sup>a</sup> 75	16	35	920	120	41	1.4
Set B	<62µm	51	<0.5	21	13	81	0.3	74	15	33	880	110	36	1.3

**Table 6.** Chemical analysis for bed sediments from the Kuskokwim River, Holitna River, Red Devil Creek, and Crooked Creek--Continued  
 [µm, micrometer; µg/g, microgram per gram; %, percent; <, less than actual value shown; microgram per gram given in dry weight basis; footnotes at end of table]

Site	Sieve fraction Bulk/<62 µm	Molyb- denum µg/g	Phos- phorus µg/g	Strontium µg/g	Arsenic µg/g	Antimony µg/g	Selenium µg/g	Mercury µg/g	Iron %	Manga- nese µg/g	Alum- inum %	Titanium %	Total org. carbon %	Total carbon %	Total sulfur %
<b>Kuskokwim River</b>															
<b>KR1</b>															
Set A	Bulk	<5	690	210	<sup>a</sup> 16.5	1.4	0.3	0.03	2.5	630	6.2	0.28	0.5	1.0	<0.1
Set A	<62µm	<5	1100	230	17.9	1.7	0.6	0.05	3.3	800	6.7	0.45	0.9	1.5	0.1
Set B	Bulk	<5	680	210	<sup>a</sup> 12.2	1.4	0.3	<0.01	2.5	660	6.2	0.29	0.4	1.1	<0.1
Set B	<62µm	<5	1100	230	14.0	1.8	0.5	0.06	3.3	770	6.6	0.47	0.8	1.5	0.1
<b>KR2</b>															
Set A	Bulk	<5	850	200	<sup>a</sup> 16.3	1.6	0.4	0.01	3.0	570	6.4	0.34	0.9	1.4	<0.1
Set A	<62µm	<5	1100	210	17.3	1.8	0.5	0.07	3.4	670	6.8	0.45	1.2	1.7	0.1
Set B	Bulk	<5	870	200	<sup>b</sup> 22	2.4	0.5	<sup>a</sup> 0.20	3.2	640	6.7	0.36	0.9	1.2	<0.1
Set B	<62µm	<5	1100	220	24	1.9	0.5	0.07	3.6	740	6.9	0.45	0.9	1.5	<0.1
<b>KR3</b>															
Set A	Bulk	<5	990	190	<sup>b</sup> 24	1.6	0.6	0.06	3.5	730	6.8	0.37	1.3	1.7	<0.1
Set A	<62µm	<5	1200	200	24	1.7	0.6	0.02	3.7	780	6.8	0.42	1.3	1.7	<0.2
Set B	Bulk	<5	1000	190	<sup>b</sup> 24	2.1	0.6	0.05	3.5	730	6.7	0.37	1.3	1.7	<0.1
Set B	<62µm	<5	1200	200	25	1.8	0.7	0.09	3.7	810	6.9	0.43	1.3	1.7	0.1
<b>KR4A Left bank</b>															
Set A	Bulk	<5	880	160	<sup>b</sup> 18.5	6.0	0.3	<sup>b</sup> 0.66	2.7	510	6.3	0.32	0.8	0.7	<0.1
Set A	<62µm	<5	1100	170	20	4.8	0.5	0.64	3.3	700	6.6	0.48	1.4	1.5	<0.1
Set B	Bulk	<5	810	170	<sup>b</sup> 18.1	4.3	0.4	<sup>a</sup> 0.28	2.8	540	6.4	0.34	0.8	0.8	<0.1
Set B	<62µm	<5	1200	180	19.1	4.3	0.4	0.48	3.2	700	6.5	0.50	1.2	1.4	<0.1
<b>KR4A Right bank</b>															
Set A	Bulk	<5	780	190	<sup>a</sup> 15.3	1.3	0.3	0.04	2.8	640	6.4	0.35	0.5	0.7	<0.1
Set A	<62µm	<5	1200	210	21	2.1	0.5	0.10	3.5	850	6.8	0.52	1.0	1.4	0.1
Set B	Bulk	<5	810	190	<sup>a</sup> 16.7	1.4	0.3	0.04	2.9	640	6.6	0.35	0.6	0.9	<0.1
Set B	<62µm	<5	1200	210	18.7	1.8	0.5	0.08	3.5	820	6.8	0.49	1.0	1.4	0.1
<b>KR5 Left bank</b>															
Set A	Bulk	<5	830	190	<sup>a</sup> 13.7	1.4	0.3	0.03	2.8	570	6.5	0.33	0.5	0.8	<0.1
Set A	<62µm	<5	1300	200	17.8	1.6	0.3	0.10	3.3	750	6.5	0.52	1.0	1.3	<0.1
Set B	Bulk	<5	820	200	<sup>a</sup> 15.8	1.3	0.3	0.03	2.8	590	6.6	0.34	0.5	0.8	<0.1
Set B	<62µm	<5	1200	200	18.4	1.5	0.4	0.05	3.2	740	6.6	0.49	0.8	1.2	<0.1
<b>KR5 Right bank</b>															
Set A	Bulk	<5	790	170	<sup>b</sup> 18.0	1.2	0.4	0.07	2.9	740	6.4	0.30	1.3	1.5	<0.1
Set A	<62µm	<5	180	180	21	1.6	0.6	0.10	3.7	1000	6.7	0.43	1.7	2.0	0.1
Set B	Bulk	<5	810	170	<sup>b</sup> 18.0	1.6	0.4	0.05	3.0	770	6.4	0.31	1.2	1.5	<0.1
Set B	<62µm	<5	1100	180	20	1.6	0.7	0.06	3.7	1000	6.7	0.43	1.7	2.1	0.1
<b>KR6</b>															
Set A	Bulk	<5	890	170	<sup>b</sup> 21	1.5	0.4	0.05	3.1	770	6.6	0.35	1.0	1.1	<0.1
Set A	<62µm	<5	1200	180	23	1.6	0.5	0.08	3.6	940	6.8	0.46	1.3	1.5	<0.1
<b>KR7</b>															
Set A	Bulk	<5	930	170	<sup>b</sup> 23	2.2	0.5	0.06	3.4	790	6.8	0.36	1.3	1.4	<0.1
Set A	<62µm	<5	1100	180	26	1.9	0.6	0.15	3.8	900	7.0	0.43	1.3	1.6	0.1
Set B	Bulk	<5	930	170	<sup>b</sup> 23	1.4	0.5	0.06	3.4	790	6.8	0.36	1.2	1.3	<0.1
Set B	<62µm	<5	1100	180	27	1.9	0.6	0.12	3.8	890	6.9	0.43	1.3	1.5	0.1
<b>Tributaries</b>															
<b>T1 (Holitna River)</b>															
Set A	Bulk	<5	780	140	<sup>a</sup> 11.9	0.8	0.2	0.04	2.7	600	5.8	0.32	0.7	0.8	<0.1
Set A	<62µm	<5	1200	150	17.4	1.2	0.5	0.13	3.5	840	6.4	0.45	1.7	1.8	<0.1
Set B	Bulk	<5	910	150	<sup>a</sup> 14.7	1.0	0.3	0.06	3.2	680	6.1	0.35	1.0	1.1	<0.1
Set B	<62µm	<5	1100	150	14.9	1.1	0.3	0.02	3.3	770	6.2	0.47	1.4	1.5	<0.1
<b>T2 (Red Devil Creek)</b>															
Set A	Bulk	<5	790	160	<sup>a</sup> 14.9	5.6	0.3	<sup>b</sup> 0.50	2.6	500	6.2	0.32	0.7	0.7	<0.1
Set A	<62µm	<5	1200	180	18.1	4.7	0.5	0.77	3.3	700	6.7	0.49	1.3	1.4	<0.1
Set B	Bulk	<5	1200	200	<sup>b</sup> 3180	5680	0.4	<sup>b</sup> 150	4.4	2600	6.1	0.32	2.6	2.1	0.1
Set B	<62µm	<5	1400	170	5150	3930	0.6	250	5.7	3800	6.0	0.39	4.9	5.1	0.1
<b>T3 (Crooked Creek)</b>															
Set A	Bulk	<5	840	140	<sup>a</sup> 15.7	1.4	0.5	<sup>a</sup> 0.26	3.4	940	6.7	0.41	3.8	3.9	0.1
Set A	<62µm	<5	790	140	16.3	1.6	0.5	0.37	3.3	950	6.9	0.43	3.6	3.7	0.1
Set B	Bulk	<5	930	160	<sup>b</sup> 17.1	1.5	0.7	<sup>a</sup> 0.30	3.6	1100	7.2	0.42	5.4	5.6	0.1
Set B	<62µm	<5	790	150	15.0	1.4	0.5	0.28	3.4	950	7.2	0.42	3.7	3.9	0.1

<sup>a</sup>Exceeds the Canadian interim freshwater sediment quality guideline (ISQG) (see table 9 later in report)

<sup>b</sup>Exceeds the Canadian probable effect limit (PEL) (see table 9 later in report)

## SPATIAL DISTRIBUTION OF CHEMICAL CONSTITUENTS

Rivers transport chemical constituents both in solution and on suspended-sediment particles. The downstream concentration and transport trends will not always mirror one another. For example, the concentration of a constituent may decrease due to mixing with waters of lower concentration, but the transport will increase due to an increased discharge. To understand the chemical transport within a river, one needs to know the concentration of the constituent (both in solution and on the suspended sediments) and the water discharge (the quantity of water flowing past a point along the river each second). Transport is determined by multiplying concentration by the discharge.

Bed sediments commonly have higher trace element concentrations than those found in water due to the presence of trace elements contained in sediment minerals or sorbed onto clays, oxides, and organic layers. Consequently, sampling the streambed sediments increases the likelihood that trace concentrations of chemical constituents in the environment will be detected. In addition, the relation between water and the sediment chemistry is dynamic, and determination of sediment chemistry is a critical component in understanding geochemical cycling.

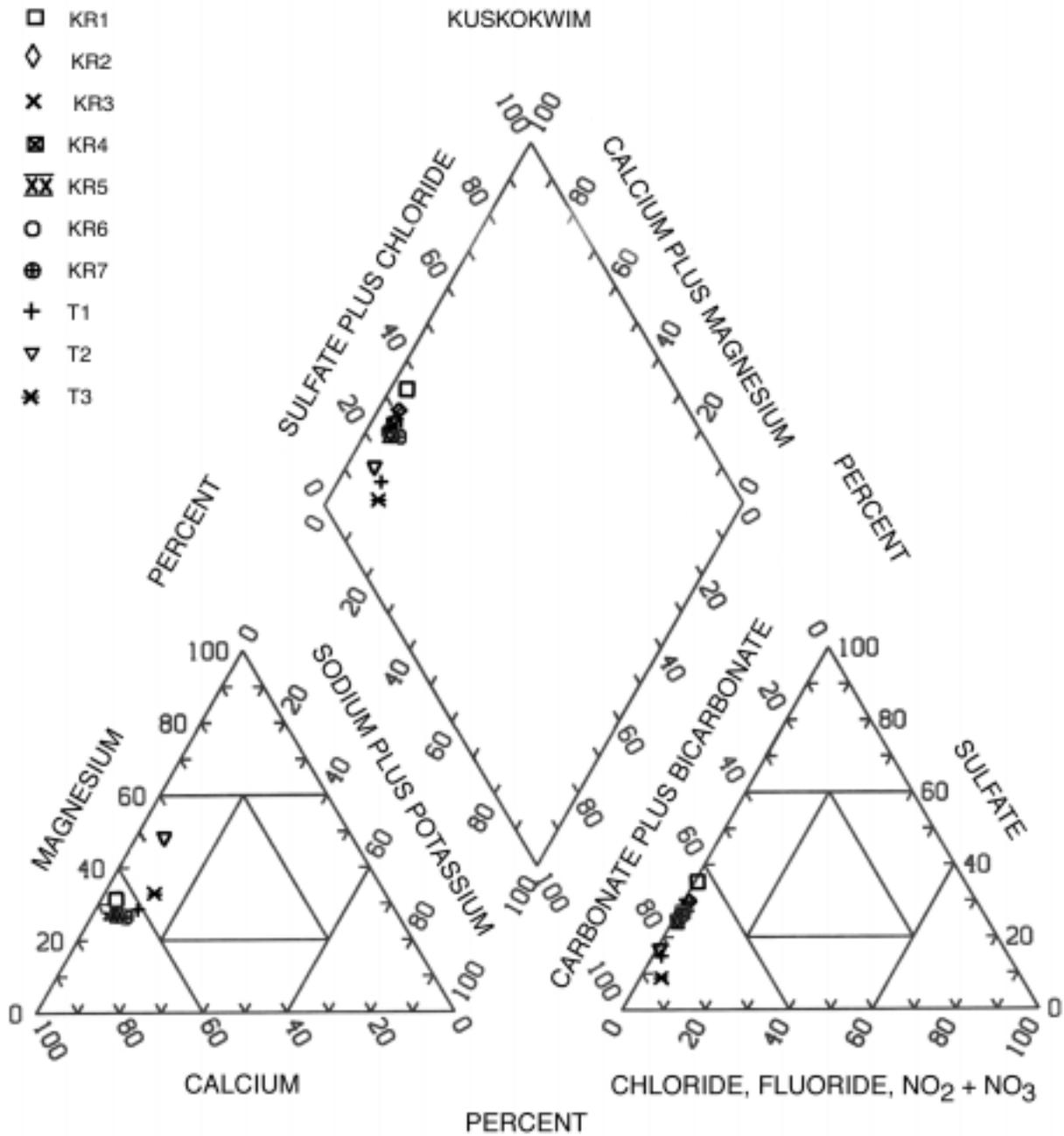
### Water

The Kuskokwim River, Holitna River, Crooked Creek, and Red Devil Creek are calcium to calcium magnesium bicarbonate waters (fig. 2). The calcium and magnesium concentrations decreased down the main stem of the Kuskokwim, as did the bicarbonate and sulfate concentrations (fig. 3). However, calcium, magnesium, bicarbonate, and sulfate transport increased, mirroring the increased water discharge (figs. 3 and 4). The calcium,

magnesium, bicarbonate, and sulfate concentrations were lower in the Holitna River, Crooked Creek, and Red Devil Creek than in the main stem (table 4), but the relative proportion of magnesium to the cation charge was higher in Crooked and Red Devil Creeks than in the main stem (fig. 2).

Dissolved trace elements boron, iron, strontium, manganese, aluminum, and barium were detected in water samples (table 4). Cadmium, cobalt, lead, nickel, silver, vanadium, selenium, uranium, and lithium concentrations were below the detection limit in all samples (Benson and others, 1998). In addition, mercury was detected in all aqueous samples because low-level analytical techniques were used (table 7). With the exception of iron and manganese, the concentrations of these trace elements were lower in the Holitna River (site T1) than in the Kuskokwim River (table 4).

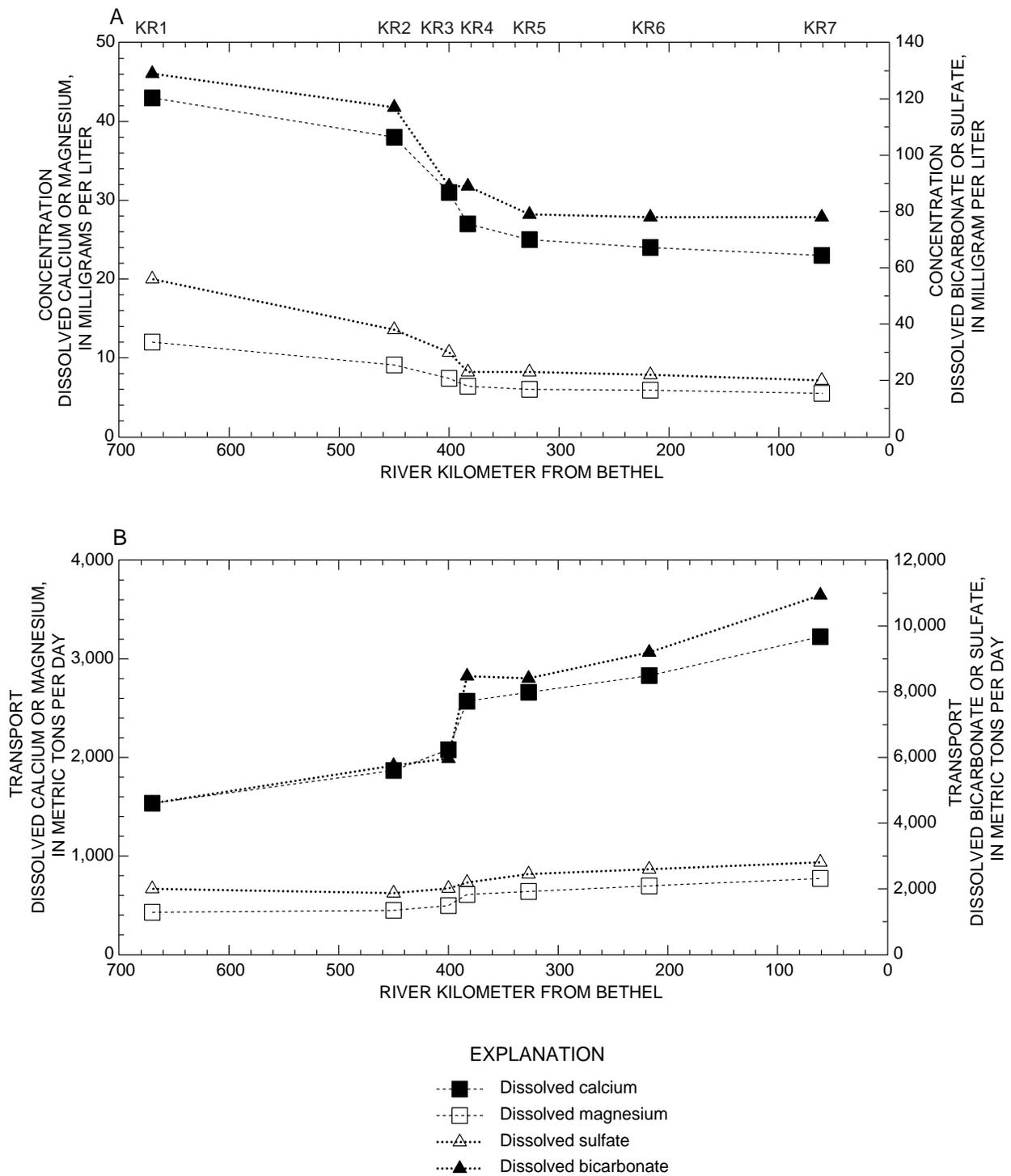
In the Kuskokwim River, dissolved-iron concentrations increase downstream from McGrath (site KR1) and peak at Crooked Creek (site KR5). The dissolved-iron concentrations in the Holitna River (site T1) and Crooked Creek (site T3) are about four times greater than those in the Kuskokwim River or Red Devil Creek (site T2) (fig. 5A). Transport depends on both the water discharge as well as the concentration; therefore, because of its greater discharge, the Holitna River (site T1, table 2) transports an order-of-magnitude more iron than Crooked Creek (site T3) (fig. 5B). The amount of dissolved iron transported by the Kuskokwim River doubles downstream from its confluence with the Holitna River, and the primary source of the dissolved iron in the lower Kuskokwim River is the Holitna River (fig. 5B). Finely divided ferruginous materials are found in both the graywacke and shale of the Kuskokwim Group. In the graywacke, the smaller fragmental constituents are stained with the ferruginous material, giving a false appearance of a limonite cement between the



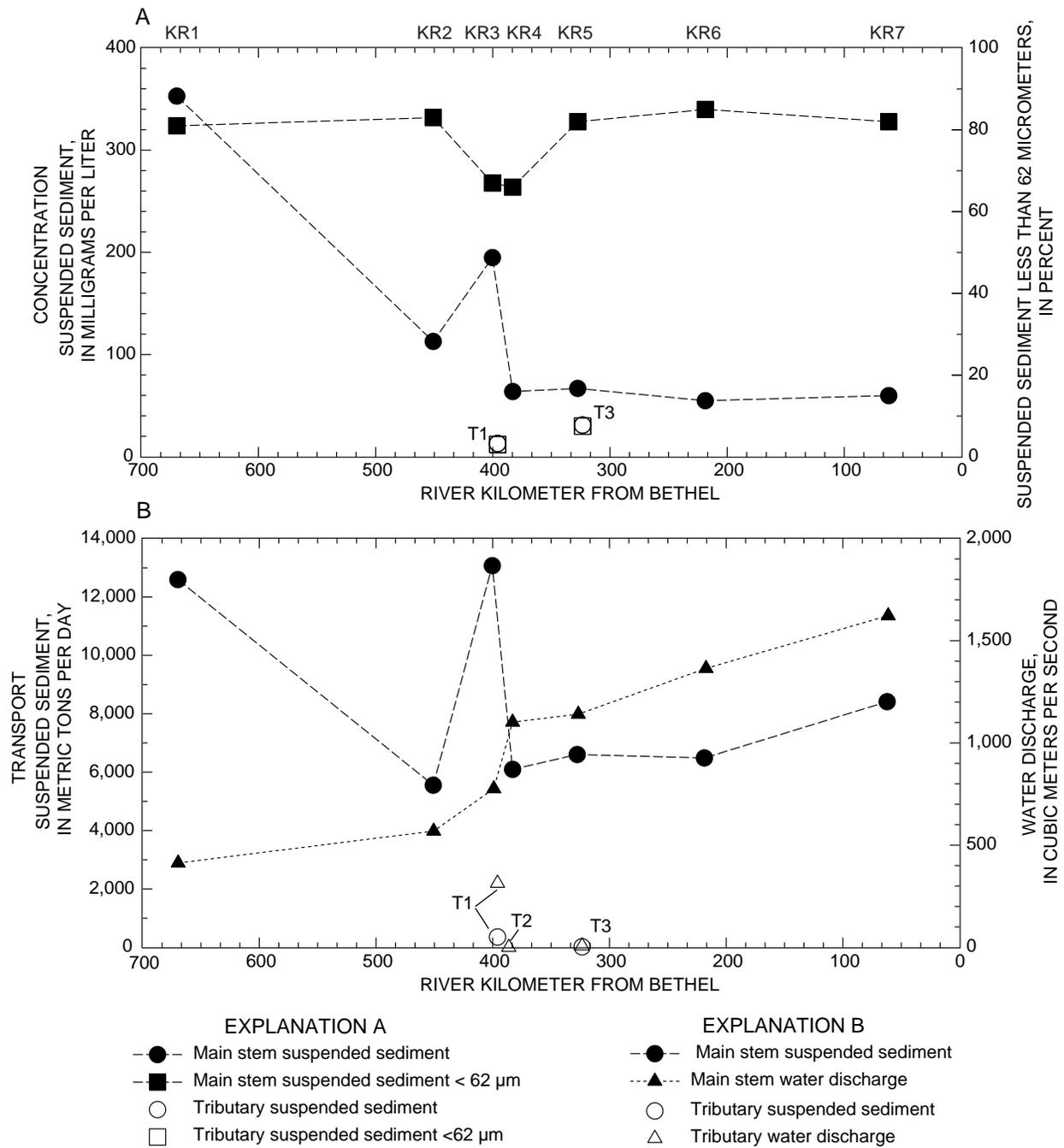
**Figure 2.** Trilinear diagram for samples taken from the Kuskokwim River, Holitna River, Crooked Creek, and Red Devil Creek.

coarse fragments, and finely divided clay particles seem to contain the ferruginous material in the shale (Cady and others, 1955). The Kusko-

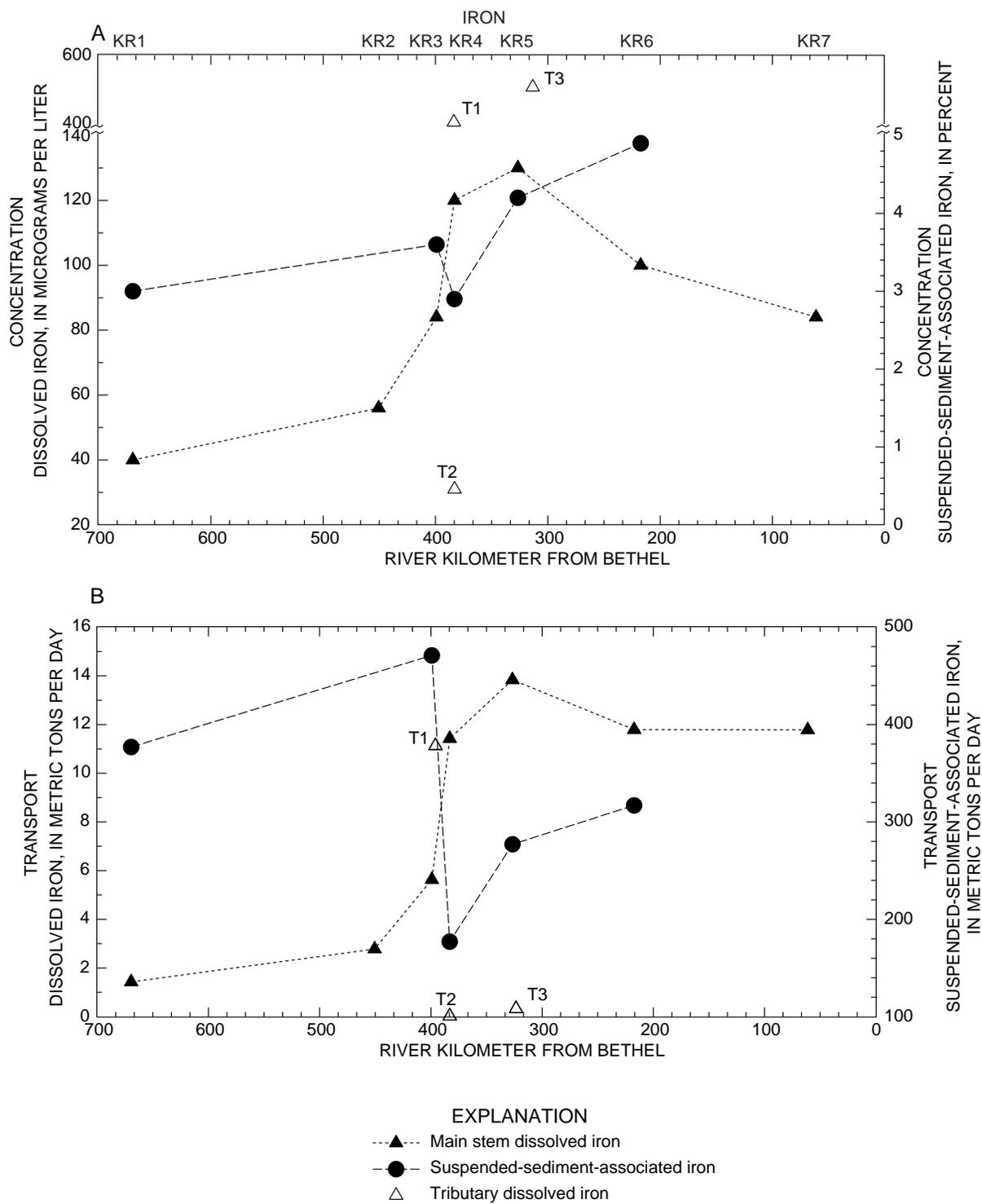
wkim Group located in the headwaters of the Holitna River is a probable source of the iron in the environment.



**Figure 3.** Calcium, magnesium, sulfate, and bicarbonate concentrations (A) and transport (B) in the Kuskokwim River main stem and tributaries.



**Figure 4.** Suspended-sediment concentration (A), and transport and water discharge (B) in the Kuskokwim River main stem and tributaries.



**Figure 5.** Dissolved and suspended-sediment-associated concentration (A) and transport (B) of iron in the Kuskokwim River main stem and tributaries.

**Table 7.** Mercury and methyl mercury data for water, suspended-sediment, and bed-sediment samples from the Kuskokwim River, Holitna River, Red Devil Creek, and Crooked Creek

[ng/L, nanogram per liter; µg/g, microgram per gram; ng/g, nanogram per gram, --, data not available or not applicable]

Site	Water samples				Suspended-sediment associated samples		Bed-sediment samples		
	Total mercury (ng/L)	Dissolved mercury (ng/L)	Total methyl mercury (ng/L)	Dissolved methyl mercury (ng/L)	Mercury (µg/g) <sup>a</sup>	Mercury (ng/L) <sup>b</sup>	Average total mercury, bulk (µg/g) <sup>a</sup>	Average total mercury, <62 µm (µg/g) <sup>a</sup>	Bulk, methyl mercury (ng/g) <sup>a</sup>
<b>Kuskokwim River</b>									
KR1	9.7	--	<0.06	--	0.05	18	0.03	0.06	0.08
KR2	5.6	--	<0.06	--	--	--	0.11	0.07	--
KR3	5.0	1.2	<0.06	<0.06	0.07	14	0.06	0.05	0.25
KR4A									
Right bank	--	--	--	--	--	--	0.04	0.09	0.12
Left bank	--	--	--	--	--	--	0.47	0.56	0.24
KR4	1.9	--	<0.06	--	0.05	3	--	--	--
KR5	3.8	1.2	<0.06	0.06	0.06	4	--	--	--
Right bank	--	--	--	--	--	--	0.06	0.08	0.08
Left bank	--	--	--	--	--	--	0.03	0.08	--
KR6	3.5	--	<0.06	--	0.09	3	0.05	0.08	--
KR7	3.5, 4.0	--	<0.06, <0.06	--	--	--	0.06	0.15	0.25
<b>Tributaries</b>									
T1	1.7	--	<0.06	--	--	--	0.05	0.08	0.24
T2	243, 230	--	0.31, 0.32	--	--	--	<sup>c</sup> 150, 0.5	<sup>c</sup> 250, 0.77	1.75
T3	10.5	--	0.49	--	--	--	0.28	0.33	3.12

<sup>a</sup>Dry weight basis; data summarized from table 6

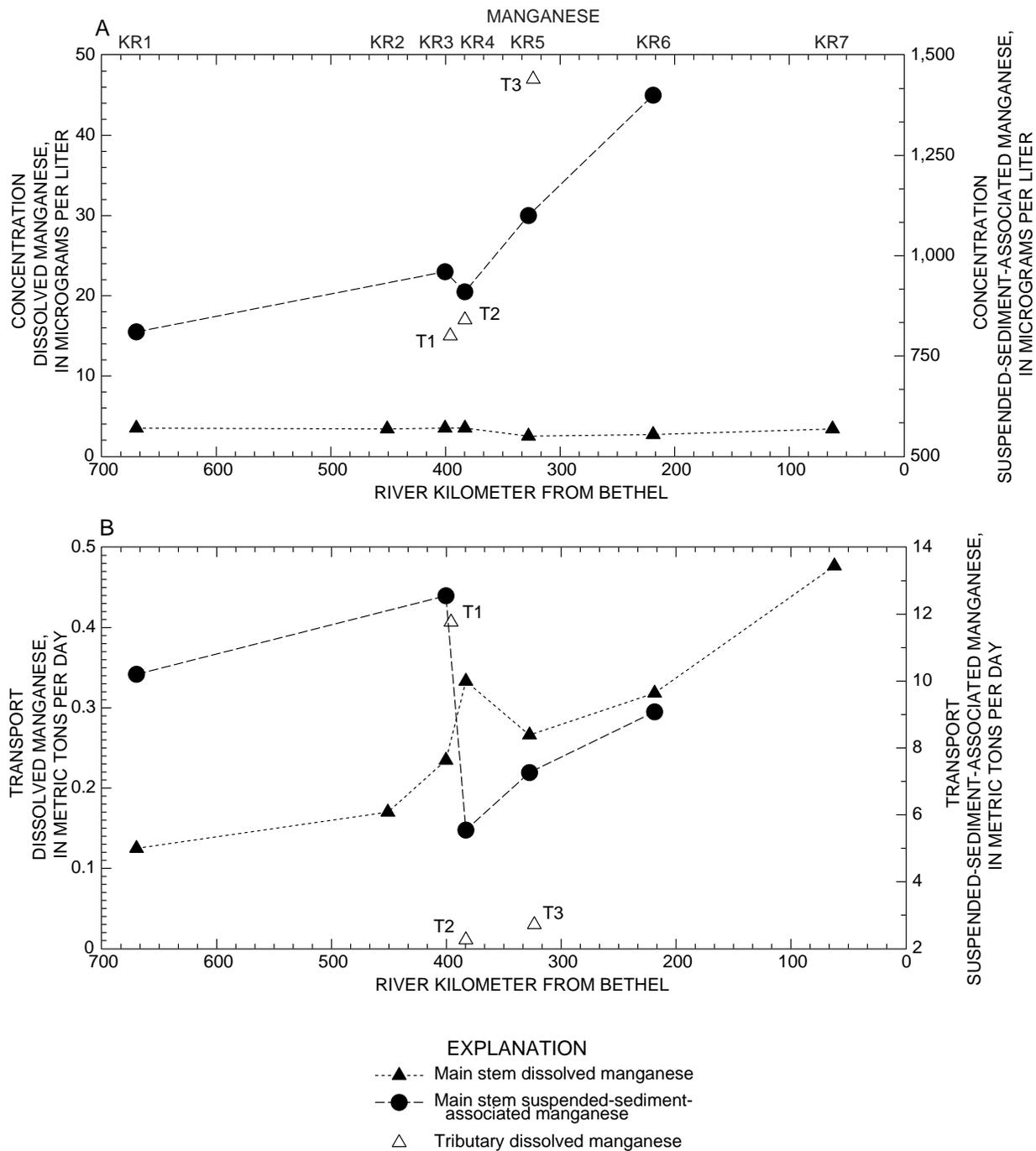
<sup>b</sup>Calculated from suspended sediment chemical analysis and suspended sediment concentration; data summarized from table 8 later in report

<sup>c</sup>Individual samples given

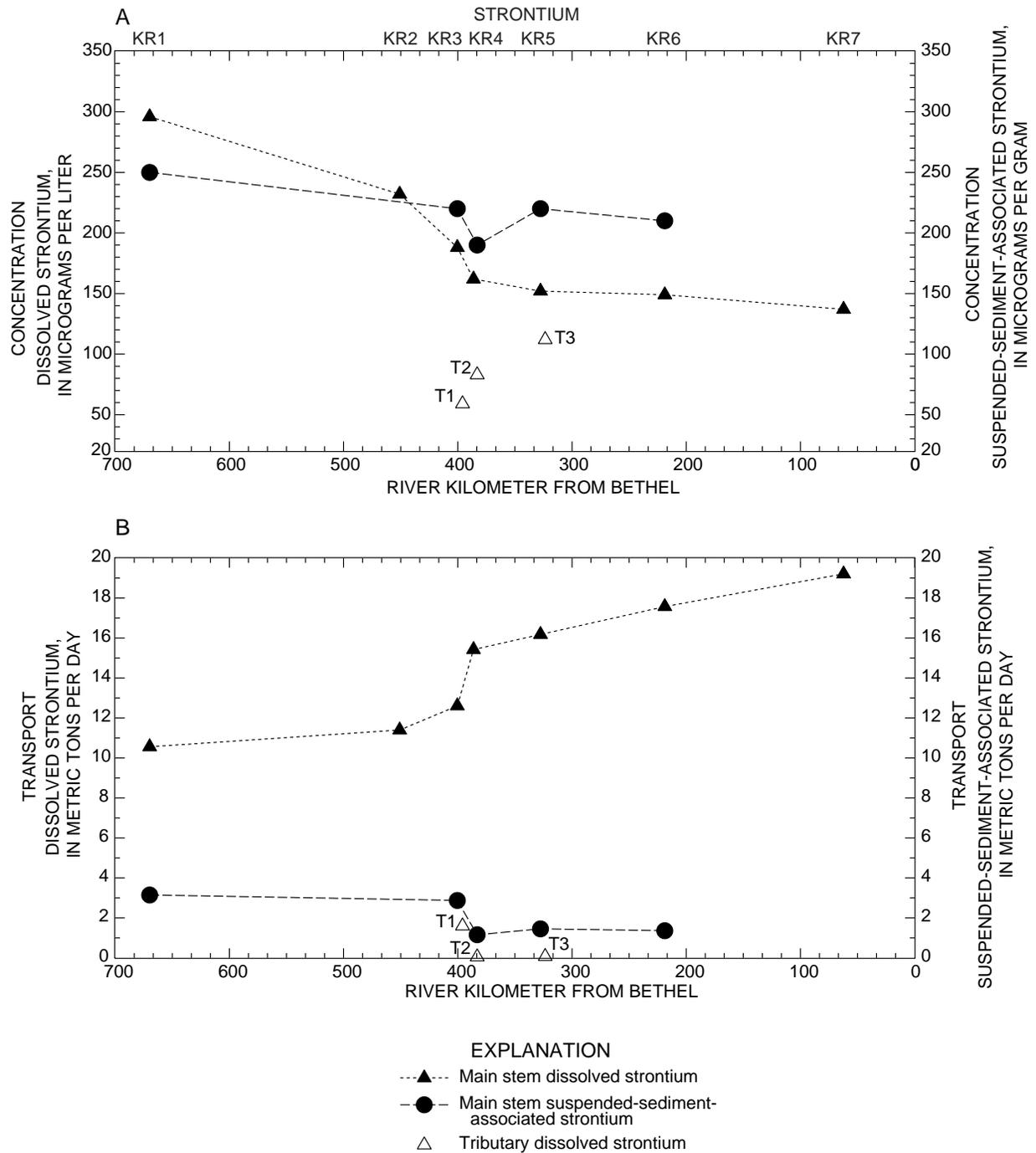
Dissolved-manganese concentrations are relatively uniform throughout the main stem of the Kuskokwim River and manganese concentrations are higher in the Holitna River, Red Devil Creek, and Crooked Creek than in the main stem, respectively (fig. 6A).

The highest concentrations of dissolved strontium and barium are found at McGrath (site KR1), and—in contrast to iron—concentrations of both elements decreased downriver (figs. 7 and 8). The lowest concentrations of strontium and barium were found in the Holitna River (site T1) (table 4). The concentrations of both elements decrease in the Kuskokwim River below the confluence with the Holitna River and transport reflects the increased water discharge as it

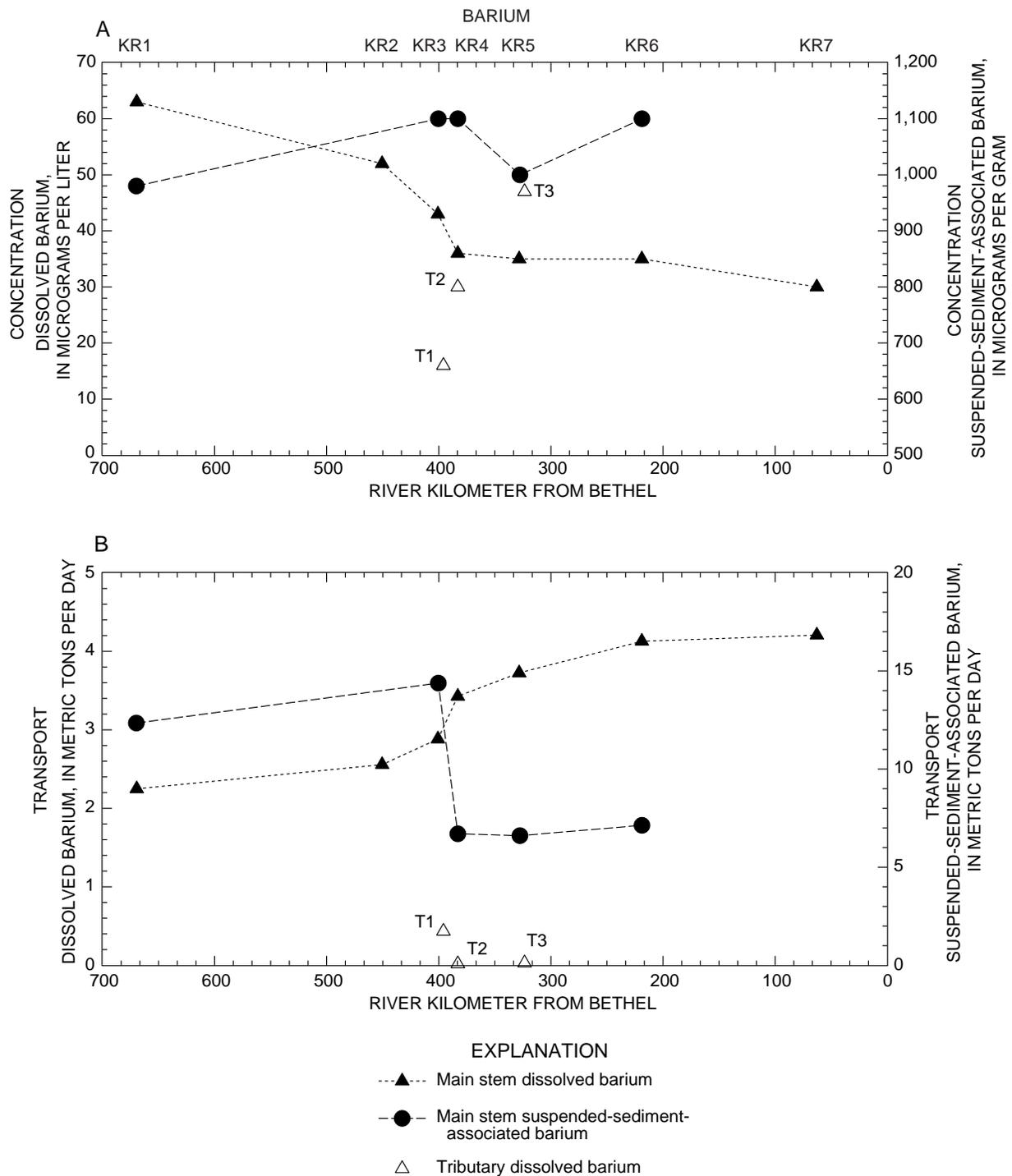
did with the major ions (fig. 3). Both strontium and barium are alkaline Earth metals as are calcium and manganese. Strontium replaces calcium or potassium in igneous-rock minerals in minor amounts, and its carbonate (strontianite) and sulfate (celesite) are common in sediments. In limestone, the strontium-calcium ratio is less than 1:1,000, although fossils in limestone tend to be enriched in strontium (Hem, 1992). Strontium concentrations similar to those in this study were found in the Mackenzie River, Canada, and were attributed to the abundant fossiliferous carbonate rocks (Reeder and others, 1972). Because no significant igneous intrusions occur within the limestone terrane of the upper basin, the probable strontium source is the limestone.



**Figure 6.** Dissolved and suspended-sediment-associated concentrations (A) and transport (B) of manganese in the Kuskokwim River main stem and tributaries.



**Figure 7.** Dissolved and suspended-sediment-associated concentrations (A) and transport (B) of strontium in the Kuskokwim River main stem and tributaries.



**Figure 8.** Dissolved and suspended-sediment-associated concentrations (A) and transport (B) of barium in the Kuskokwim River main stem and tributaries.

Mercury concentration was measured in unfiltered samples at all sites, whereas mercury concentration was analyzed in filtered samples at only two sites. Consequently, in contrast to the other elements discussed, the downriver mercury trends represent the total rather than dissolved mercury. The total mercury concentration in water samples from the Kuskokwim River ranged from 1.9 to 9.7 nanograms per liter (ng/L) and the tributary concentration ranged from 1.7 to 243 ng/L (table 7). Total mercury concentration in the main stem decreased between KR1 (670 km) and KR3 (400 km) and increased slightly from KR4 (383 km) to KR5 (327 km) (fig. 9). There is a net decrease in total mercury concentration from KR1 to KR6. The total mercury concentration is highest in Red Devil Creek (site T2) and lowest in the Holitna River (site T1) (table 7). The higher concentration from Red Devil Creek did not affect the main stem mercury concentration because the tributary was small (discharge 0.02 m<sup>3</sup>/s) relative to the Kuskokwim River (discharge 1,102 m<sup>3</sup>/s). Dissolved mercury was analyzed in two samples: one taken from the Kuskokwim River above the confluence with the Holitna River (site KR3) and the other from below the confluence (site KR5). The concentration of dissolved mercury was 1.2 ng/L in both samples (table 7). The dissolved fraction is 24 and 32 percent of the respective total mercury concentration.

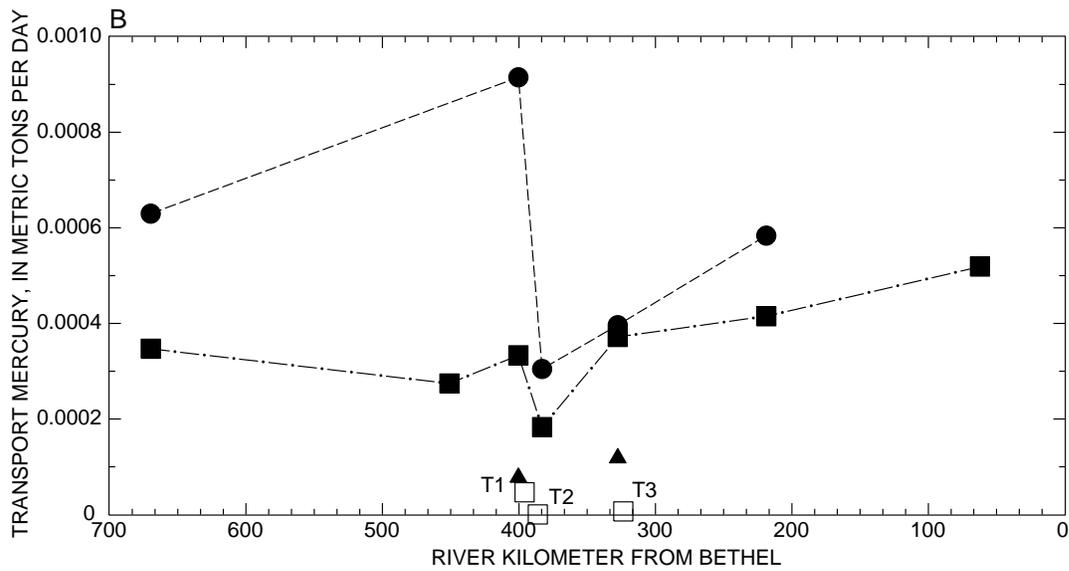
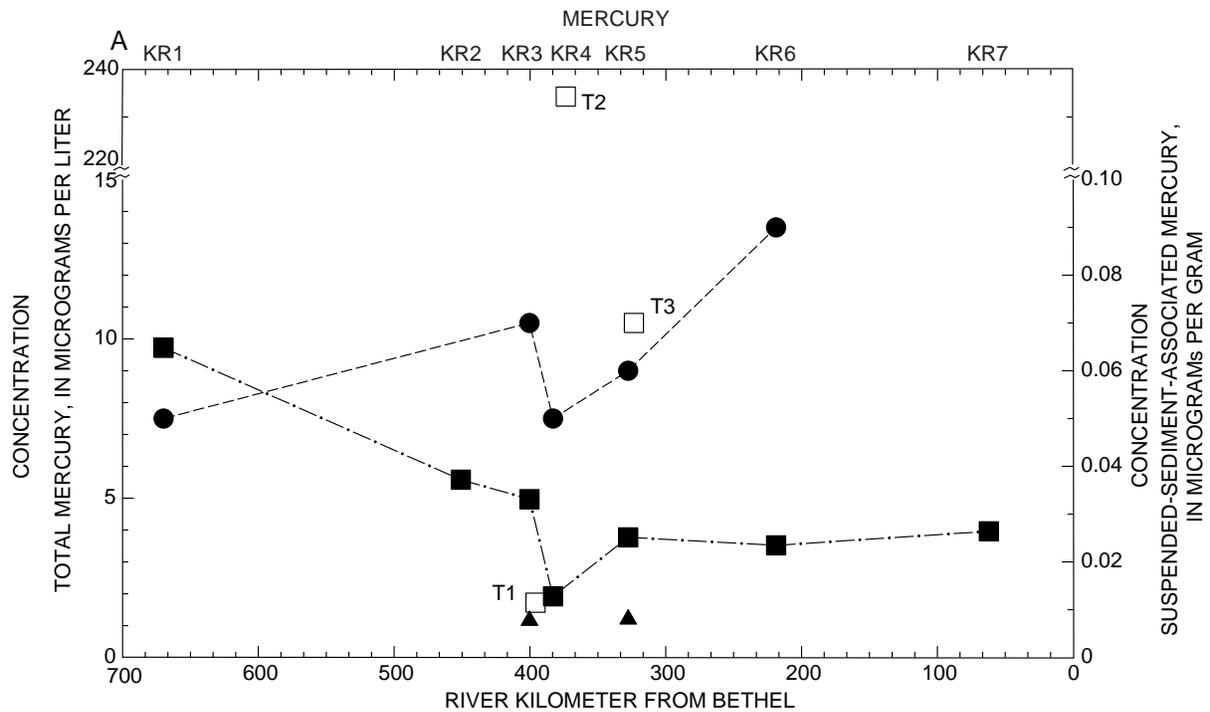
The total mercury transport exhibits a slight increase between KR1 and KR6. Mercury transport calculated from the suspended-sediment-associated mercury concentration is higher than that of the unfiltered water sample (fig. 9, table 7). This probably reflects the differences in sampling method between the samples. The suspended-sediment-associated mercury sample was a depth- and width-integrated sample, whereas the total aqueous sample was a surface width-integrated sample. Sediment concentrations can vary through the vertical water column (Horowitz, 1995), and

the near-surface width integration may not represent the total mercury transport.

Methyl mercury can accumulate in tissue and is the mercury species of greatest concern for bioaccumulation. All methyl mercury concentrations in the main stem water samples are <0.06 ng/L, but methyl mercury concentrations in Crooked Creek (site T3) and Red Devil Creek (site T2) samples are about 0.5 and 0.3 ng/L, respectively (table 7).

No samples exceeded 2 µg/L (2,000 ng/L), the U.S. Environmental Protection Agency (USEPA) drinking-water standard for mercury, but Red Devil Creek exceeded 0.012 µg/L (12 ng/L) mercury, the concentration at which aquatic life might be affected (U.S. Environmental Protection Agency, 1992). In addition to mercury, antimony (281 µg/L) and arsenic (180 µg/L) were detected in water collected from Red Devil Creek (site T2) (table 4). In these samples, dissolved arsenic concentrations exceeded 50 µg/L (table 4), the USEPA drinking-water standard for arsenic (U.S. Environmental Protection Agency, 1992).

Nutrient concentrations are generally low throughout the system (table 4). Virtually all of the nitrogen present is in the form of nitrate. Concentrations are highest at sites KR1 and KR2, but decrease throughout the mid- and lower river. Nitrate-plus-nitrite concentrations in the Holitna River (site T1) are one-fifth as great as those in the upper Kuskokwim River. Total phosphorus is greatest in the upper river and decreased downstream. Dissolved organic carbon remains uniform throughout the Kuskokwim River main stem and is twice as high in the Kuskokwim River as in the Holitna River (site T1). Crooked Creek (site T3) has the highest dissolved organic carbon concentration measured (6.8 mg/L).



EXPLANATION

- Main stem total aqueous mercury
- Main stem suspended-sediment-associated mercury
- ▲ Main stem dissolved mercury
- Tributary total mercury

**Figure 9.** Total and suspended-sediment-associated concentrations (A) and transport (B) of mercury in the Kuskokwim River main stem and tributaries.

## Suspended Sediment

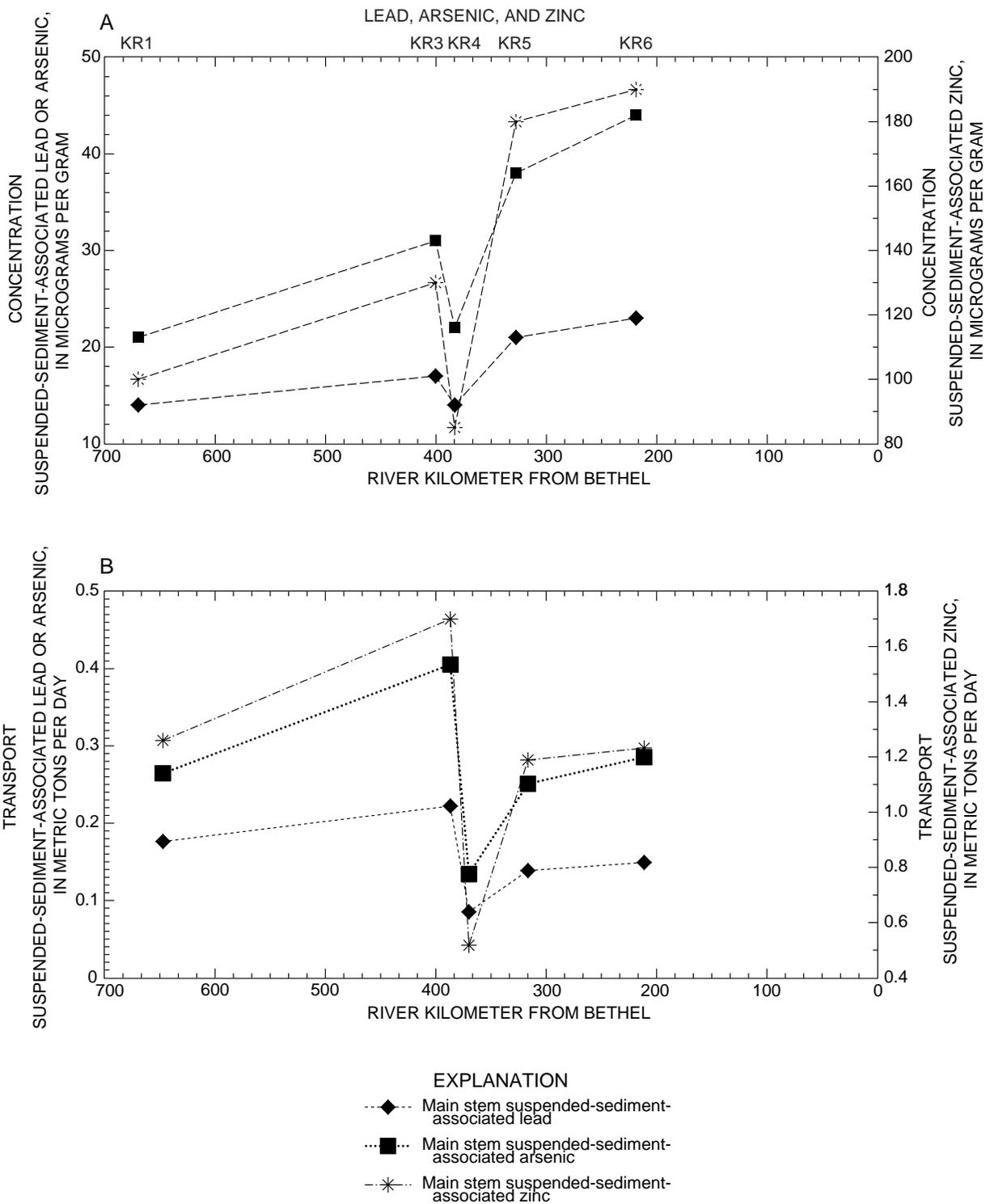
Suspended-sediment concentrations fluctuate slightly between sites KR1 to KR3, but are relatively uniform from sites KR4 to KR7. In general, total sediment concentration decreases below McGrath (fig. 4A). The concentration of the <62  $\mu\text{m}$  fraction is relatively

uniform throughout the river and accounts for between 65 and 80 percent of the total concentration. However, suspended-sediment-associated concentrations of iron, manganese, mercury, lead, arsenic, and zinc showed a net increase from site KR1 to site KR6 (table 8; figs. 5, 6, 9, and 10).

**Table 8.** Chemical analysis for suspended sediments from the Kuskokwim River

[ $\mu\text{g/g}$ , microgram per gram; %, percent; <, less than actual value shown]

Constituent	Unit (dry weight basis)	Kuskokwim River site				
		KR1	KR3	KR4	KR5	KR6
Silver	$\mu\text{g/g}$	<0.5	<0.5	<0.5	<0.5	<0.5
Copper	$\mu\text{g/g}$	31	28	21	36	40
Lead	$\mu\text{g/g}$	14	17	14	21	23
Zinc	$\mu\text{g/g}$	100	130	85	180	190
Cadmium	$\mu\text{g/g}$	0.4	0.4	0.3	0.6	0.7
Chromium	$\mu\text{g/g}$	83	76	79	96	90
Cobalt	$\mu\text{g/g}$	13	13	11	15	17
Nickel	$\mu\text{g/g}$	49	42	48	53	50
Barium	$\mu\text{g/g}$	980	1100	1100	1000	1100
Vanadium	$\mu\text{g/g}$	99	100	80	110	120
Lithium	$\mu\text{g/g}$	40	48	36	53	58
Beryllium	$\mu\text{g/g}$	1.6	1.8	1.5	1.8	1.9
Molybdenum	$\mu\text{g/g}$	<5	<5	<5	<5	<5
Phosphorus	%	710	840	780	1000	1100
Strontium	$\mu\text{g/g}$	250	220	190	220	210
Arsenic	$\mu\text{g/g}$	21	31	22	38	44
Antimony	$\mu\text{g/g}$	1.8	1.6	1.3	2.3	2.4
Selenium	$\mu\text{g/g}$	0.4	0.6	0.5	0.7	0.8
Mercury	$\mu\text{g/g}$	0.05	0.07	0.05	0.06	0.09
Iron	%	3.0	3.6	2.9	4.2	4.9
Manganese	$\mu\text{g/g}$	810	960	910	1100	1400
Aluminum	%	6.3	6.9	6.0	7.0	7.3
Titanium	%	0.29	0.32	0.24	0.35	0.38
Total organic carbon	%	0.6	1.1	1.0	2.1	2.2
Total carbon	%	1.3	1.5	1.3	2.2	2.4
Total sulfur	%	0.2	0.1	0.1	0.1	0.1



**Figure 10.** Suspended-sediment-associated lead, arsenic, and zinc concentrations (A) and transport (B) in the Kuskokwim River main stem and tributaries.

The total suspended-sediment transport in the upper river was higher than that in the lower river (fig. 4B). Transport of suspended-sediment-associated trace elements depends on the sediment transport and suspended-sediment-associated trace-element concentration. The decrease in sediment transport from site KR3 (400 km) to site KR4 (383 km) is mirrored in the transport of the associated trace elements. Transport of iron, manganese, mercury, lead, arsenic, and zinc increases from site KR4 (383 km) to site KR6 (217 km) reflecting the increased concentration of associated trace elements (figs. 5, 6, 9, 10). The transport of trace elements by suspended sediments was lower for all elements in the lower river than in the upper river, indicating storage of sediments and their associated metals within the river system (figs. 5-10).

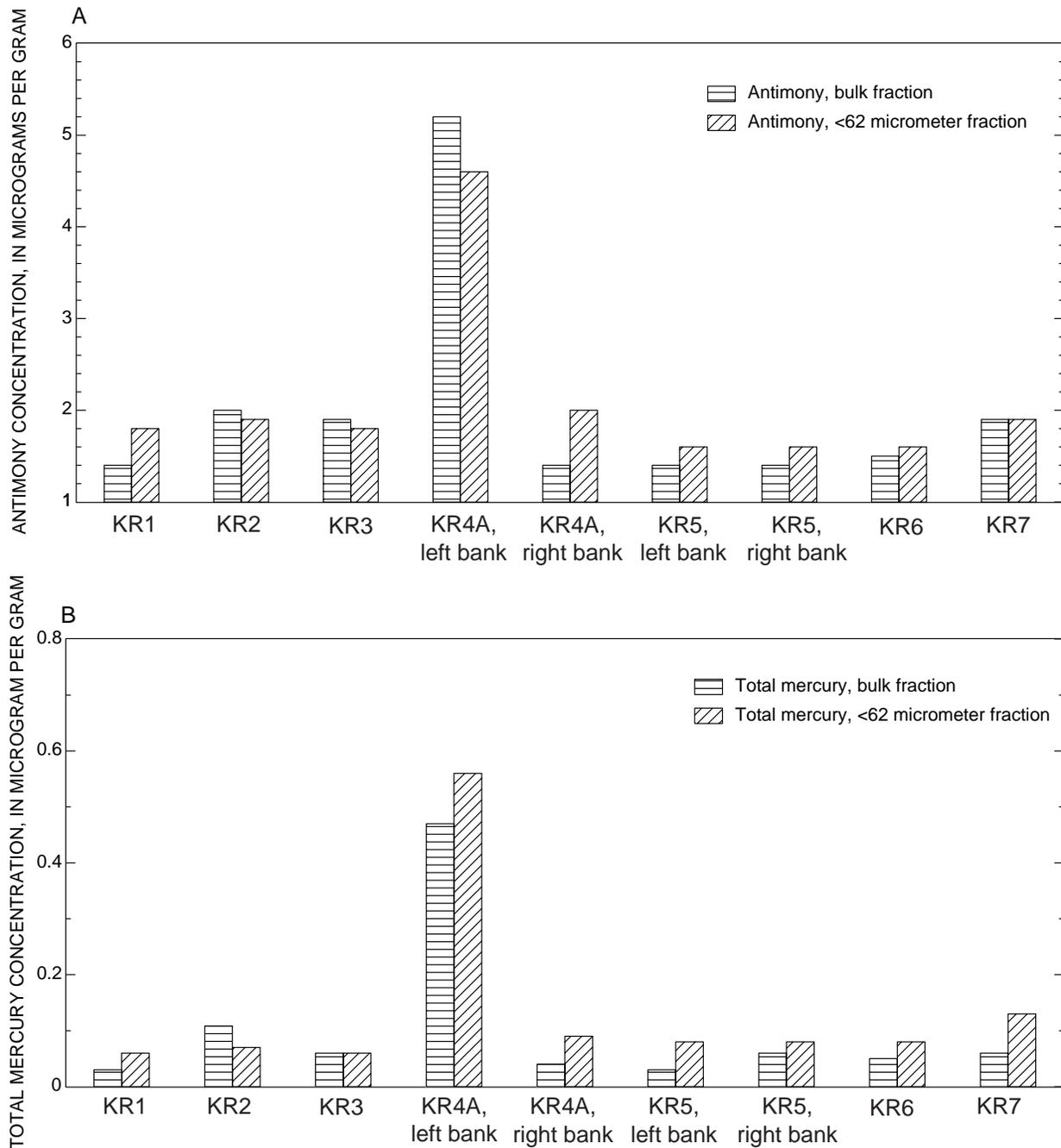
## Bed Sediment

Bed-sediment samples from the Kuskokwim River did not show the downstream concentration trends seen in the suspended sediments and showed little chemical variation between sites, except for samples taken from the left bank of site KR4A and those from site T2 (table 6). Between 15 and 59 percent of the bulk samples consisted of the <62 $\mu$ m fraction (table 6). In general, the finer fraction had slightly higher concentrations than the corresponding bulk analysis.

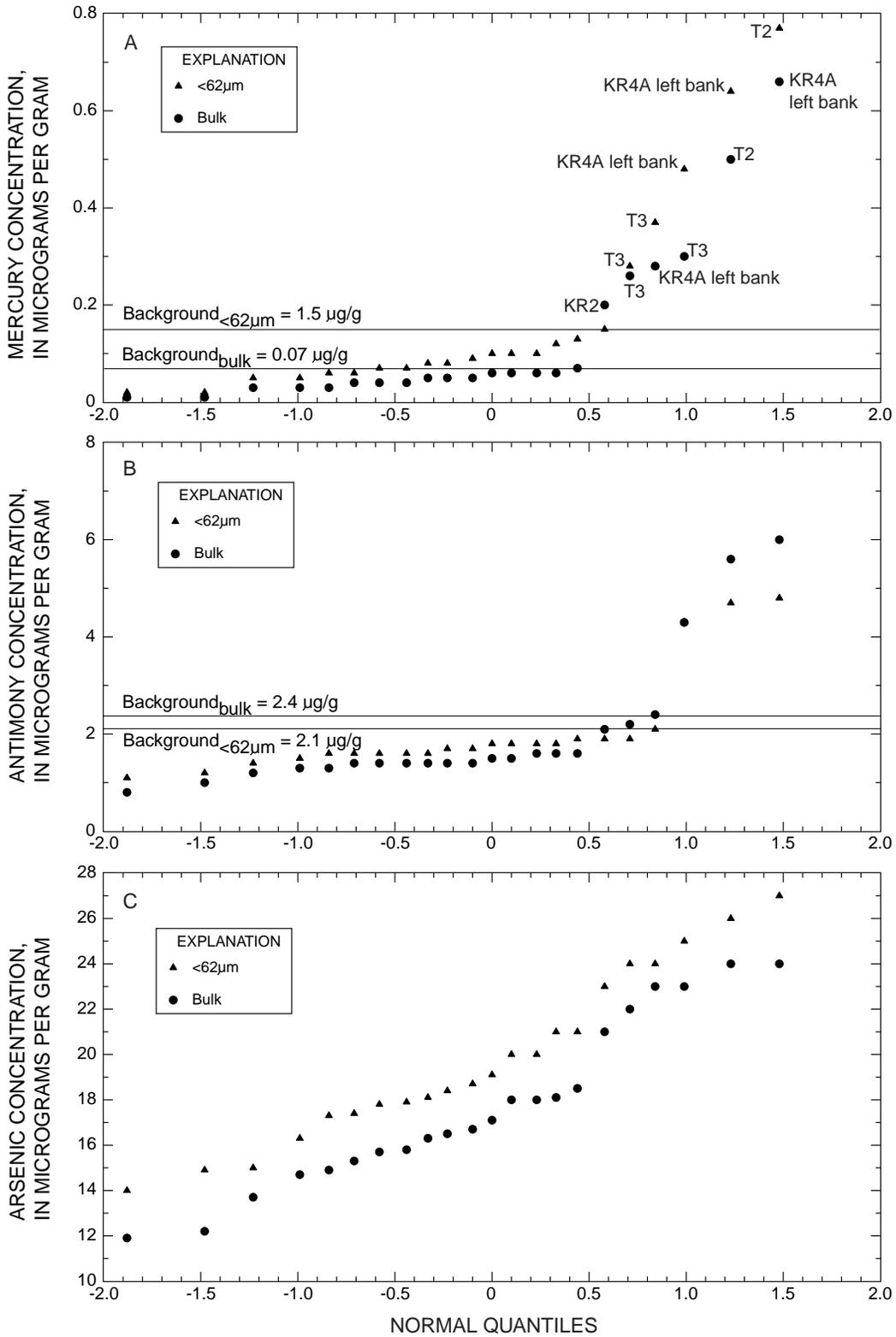
The Red Devil mercury mine operated on the left bank of the Kuskokwim River, and other mercury deposits are mapped near the river's left bank (Miller and Bundtzen, 1994). Samples were collected from both the right and left banks of the Kuskokwim River at sites KR4A and KR5 to determine if a compositional difference between banks existed. At site KR4A, a compositional difference was found in the left bank sediment samples relative to the right bank samples and the rest of the Kuskokwim River samples. No difference was found

between the left and right banks at site KR5 (fig. 11). The bed-sediment samples taken from the left bank of site KR4A had mean bulk mercury (0.47  $\mu$ g/g) and antimony (5.2  $\mu$ g/g) concentrations that were two and three times higher than those of the other Kuskokwim River samples (fig. 11). No difference was found in the arsenic concentrations of these samples (table 6).

Sample concentrations above background may be elevated because of natural weathering of a localized source or by human activities. One approach to evaluating the degree to which a sample is elevated is to determine a basin-specific background concentration (Velz, 1984; Deacon and Stephens, 1998). Samples can then be compared to the background concentration to determine their degree of elevation over background. Probability plots for mercury, antimony, and arsenic were developed to determine the basin-specific background. Plots for mercury and antimony showed sharp slope breaks for both the bulk sample and the <62  $\mu$ m fraction, but arsenic did not (fig. 12). The shape of the mercury and antimony plot indicates the presence of points that depart from the underlying trend (Helsel and Hirsch, 1992). Trace-element concentrations in bed sediments are affected by particle size; consequently, the bulk sample and <62  $\mu$ m fraction give slightly different background concentrations. Mercury background concentrations were 0.09  $\mu$ g/g and 0.15  $\mu$ g/g for the bulk and <62  $\mu$ m samples, respectively. These concentrations agree with the background concentration range found for non-source areas of 0.06 to 0.1  $\mu$ g/g mercury reported by Nelson and others (1977). Antimony background concentrations were 1.6  $\mu$ g/g and 2.1  $\mu$ g/g for the bulk and <62  $\mu$ m samples, respectively. Because arsenic showed no clear break in slope, a background concentration was not defined but would be greater than 27  $\mu$ g/g. However, Gray and others (1991) found that the combination of mercury, antimony, and arsenic concentrations greater than 3  $\mu$ g/g, 1  $\mu$ g/g, and 15  $\mu$ g/g, respectively, were



**Figure 11.** Average antimony (A) and total mercury (B) concentrations in bed-sediment samples taken from the Kuskokwim River.



**Figure 12.** Probability plots of mercury, antimony, and arsenic concentrations in the Kuskokwim River basin bed sediments relative to a normal distribution.

indicative of upstream cinnabar-stibnite. This would imply lower antimony and arsenic concentrations and, possibly, a higher mercury background than were found in this study. The discrepancy could be due to differences in the particle sizes of the bed sediment between the studies and to a greater focus on drainages with mercury deposits in Gray's study.

Samples from site T2 and from the left bank at site KR4A exceed the background concentrations for mercury and antimony in both the bulk sample and <62 µm fraction. The variability between the Red Devil Creek bed-sediment samples was high, despite side-by-side collection and sample compositing (table 6), and may be due to finely divided ore minerals with a patchy dispersal distribution. Samples from site T3 exceeded the background concentration for mercury in both the bulk sample and the <62 µm fraction, and one sample from KR2 exceeded the background concentration for a bulk sample. The mercury concentrations reported here for site T3 are about twice those previously reported for Crooked Creek (Gray and others, 1994). Once again, this difference may be due to differences in bed-sediment particle size. The source of the mercury in Crooked Creek (site T3) is unclear, but may be related either to the upstream mineralogy or to past placer mining activity (Gray and others, 1994). The concentrations of mercury and antimony found at site T2 and on the left bank of site KR4A likely reflect the proximity of the mercury ore deposits and past mining activity.

There are no State or Federal guidelines or standards for trace-element concentrations in streambed sediments with which the Kuskokwim River data can be compared. However, the Canadian Council of Ministers of the Environment (1999) have adopted "*Canadian Sediment Quality Guidelines for the Protection of Aquatic Life*." Guidelines have been set for arsenic, cadmium, chromium, copper, lead, mercury, and zinc. Two levels are defined for the total concentration in a bulk sediment sam-

ple: (1) the interim sediment quality guideline (ISQG), where toxicological effects are expected to be rare, and (2) the probable effect level (PEL), where toxicological effects are expected to occur (table 9) (Canadian Council of Ministers for the Environment, 1999).

**Table 9.** Interim freshwater sediment quality guidelines (ISQGs) and probable effect levels (PELs; dry weight)

{Guidelines from Canadian Council of Ministers for the Environment, 1999; mg/kg, milligram per kilogram}

Constituent	ISQG (mg/kg) <sup>a</sup>	PEL (mg/kg) <sup>a</sup>
Arsenic	5.9	17.0
Cadmium	0.6	3.5
Chromium	37.3	90.0
Copper	35.7	197
Lead	35.0	91.3
Mercury	0.17	0.486
Zinc	123	315

<sup>a</sup>Equivalent to microgram per gram (µg/g)

All bed-sediment samples from the Kuskokwim River basin exceed the ISQG for arsenic and chromium, and about one-half exceed the PEL for arsenic (table 6). One sample from Red Devil Creek exceeds the PEL for arsenic by two orders of magnitude and slightly exceeds the PEL for chromium (table 6). Four samples—one from KR2, one from KR4A, and two from T3—exceed the ISQG for mercury. One sample from KR4A and both samples from T2 exceed the PEL for mercury. Mercury concentrations in the Kuskokwim River bed sediments fell within the 50<sup>th</sup> percentile (40 ng/g, 0.04 µg/g) and 75<sup>th</sup> percentile (80 ng/g, 0.08 µg/g) of the mercury distribution found for 61,744 streambed sediments in Canada (Rasmussen and others, 1998). Exceptions were one sample from site KR2, which fell between the 75<sup>th</sup> and 95<sup>th</sup> percentile (199 ng/g, 0.199 µg/g), and those from the left bank at site KR4A, which fell above the 95<sup>th</sup> percentile.

Methyl mercury in bed sediments was highest in sediment taken from sites T3 (3.12 ng/g) and T2 (1.75 ng/g) (table 7). Main stem methyl mercury concentrations ranged from 0.08 to 0.25 ng/g and showed no downstream trend.

## SUMMARY

The purpose of this study was to evaluate the water quality of the Kuskokwim River and selected tributaries by determining the chemical composition of the river in relation to lithologic changes. Of particular interest was the distribution of mercury within the Kuskokwim River because of the past mining history and the continued interest in the mineral resources of the river basin. Both the weathering of the mercury-rich ore deposits and the past mining activity could contribute mercury and associated metals to the Kuskokwim River. Seven sites along the Kuskokwim River and three tributaries were sampled for water, suspended-sediment, and bed-sediment chemistry. Sites were selected to bracket both the major lithologic changes and the mining regions of the Kuskokwim River. Sites were sampled sequentially in downstream order in a manner that attempted to sample the same parcel of water. This method enabled changes in downstream changes to be identified.

Lithologic changes in the Kuskokwim River basin are reflected in the iron and strontium concentrations of the river. The dissolved iron transported by the Kuskokwim River doubles below the confluence with the Holitna River. Graywacke and shale, containing finely divided ferruginous materials, are prevalent in the headwaters of the Holitna River and are the most likely source of the iron. In contrast, the strontium concentration is lower in the Holitna River than in the Kuskokwim River. The limestone of the upper basin is the probable source for strontium. Storage of suspended-sediment and the associated trace elements occurs within

the river, as is indicated by their higher transport in the upper river than in the lower river.

Total mercury concentrations at all sites were below the USEPA drinking-water criteria, but mercury at Red Devil Creek exceeded the concentration that may affect aquatic life. However, because its discharge is small relative to that of the Kuskokwim River, Red Devil Creek does not increase the mercury concentration in the Kuskokwim River. All bed sediments throughout the basin exceeded the Canadian ISQG for arsenic and chromium, and about one-half exceeded the PEL for arsenic. One sample from Red Devil Creek exceeded the PEL for arsenic by two orders of magnitude and slightly exceeded the PEL for chromium. Four samples—one from KR2, one from KR4A, and two from T3—exceeded the ISQG for mercury. One sample from KR4A and both samples from T2 exceeded the PEL for mercury.

Mercury and antimony background concentrations were slightly different depending on whether they were determined from the bulk sample or from the <62  $\mu\text{m}$  fraction. Mercury background concentrations are 0.09  $\mu\text{g/g}$  and 0.15  $\mu\text{g/g}$  for the bulk and <62  $\mu\text{m}$  samples, respectively. Antimony background concentrations are 1.6  $\mu\text{g/g}$  for the bulk and 2.1  $\mu\text{g/g}$  for the <62  $\mu\text{m}$  samples. The arsenic background concentration was not defined but would be greater than 27  $\mu\text{g/g}$ . Samples from site T2 and the left bank at site KR4A were elevated relative to background concentrations for mercury and antimony. The elevated mercury and antimony concentrations at these sites are likely due to the presence of the ore body and past mining activities. Mercury concentrations about twice as high as background concentrations were also found at site T3. The origin of this elevated mercury concentration is unclear, but could be from either the upstream mineralogy or past placer mining activity.

Methyl mercury is the form of mercury that is most readily bioaccumulated within

aquatic environments. Methyl mercury was detected in water samples only from sites T2 and T3. These sites also had the highest methyl mercury concentrations detected in bed sediment and were 1.75 ng/g and 3.12 ng/g for sites T2 and T3, respectively. In contrast, the methyl mercury concentrations in bed sediments collected from the Kuskokwim River ranged from 0.08 to 0.25 ng/g.

The chemical distribution within a river system is best evaluated by collecting and analyzing multiple sampling media rather than a single sampling medium. Sediments commonly have higher concentrations of chemical constituents than the water it is in contact with has, as was the case in this study. Sampling bed sediments and suspended sediments for chemical analysis, in addition to the water, provided a more complete description about the spatial distribution and chemical transport within the Kuskokwim River.

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