

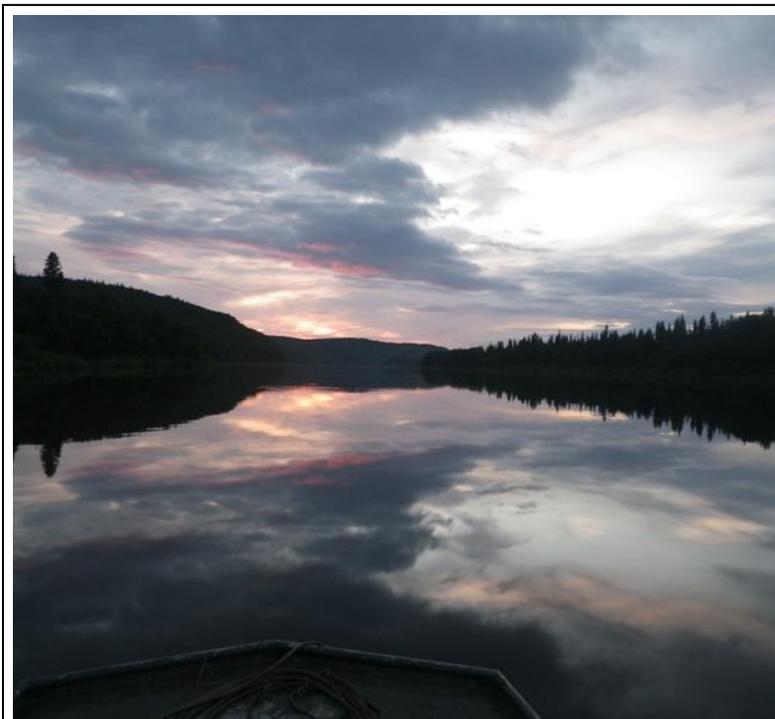
Bureau of Land Management
U.S. Department of the Interior

Alaska State Office
Division of Resources, Lands, and Planning
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Final Operations Plan - 2010

Quantification of potential contaminants with particular emphasis on methyl mercury in fish and aquatic macroinvertebrate tissues in the middle Kuskokwim River, Alaska.



ON THE COVER

Upper Left: Holitna River. *Upper Right:* Dolly Varden sampled from McCally Creek.

Middle Right: Project leader sorting macroinvertebrates.

Bottom: Northern pike from a slough on the Holitna River.

Photographs by: Bureau of Land Management staff

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1.0 Introduction

The Kuskokwim River drains a significant area of southwestern Alaska and supports a variety of resident and anadromous fish species. Subsistence uses of the land and wildlife have long sustained the peoples of the central Kuskokwim River basin in western Alaska (Brelsford et al. 1987). Within the last decade, increasing concerns associated with environmental contaminants and Alaska's fish and wildlife have prompted the State of Alaska and various federal agencies to initiate monitoring programs. As a result of these efforts, an improved understanding of contaminants, such as methylmercury, within freshwater and anadromous fish species and the potential causal factors have been realized. Specifically in the Kuskokwim River basin, which is within what is often referred to as "the mercury belt" in Alaska, a number of mineral deposits have been mapped, that contain mercury (Hg), arsenic, antimony and other metals (Sainsbury and MacKevett, 1965). Some of these deposits were mined during the early and mid-20th century and remnant waste rock and processed ore from these operations are still present at some locations.

Resident fish species in the Kuskokwim and at least one tributary have been shown to contain elevated levels of mercury (Gray et. al, 2000). The relative contributions of mercury to the Kuskokwim ecosystem by abandoned mines is not well understood. The middle Kuskokwim River, between Crooked Creek and Stony River runs through an area containing a number of known mercury deposits. The potential impacts of the mercury deposits on the aquatic food web, including species targeted for subsistence harvest, have not been thoroughly explored. Metals data collected from representative species at several trophic levels are needed to estimate the natural loading of bioaccumulated metals in the aquatic ecosystem. This project seeks to collect the data needed to estimate natural levels of metals in sediments, water and levels of bioaccumulation across the trophic spectrum of the aquatic biota. Study results will provide a more complete understanding of metals bioaccumulation in the aquatic food web along the Kuskokwim River.

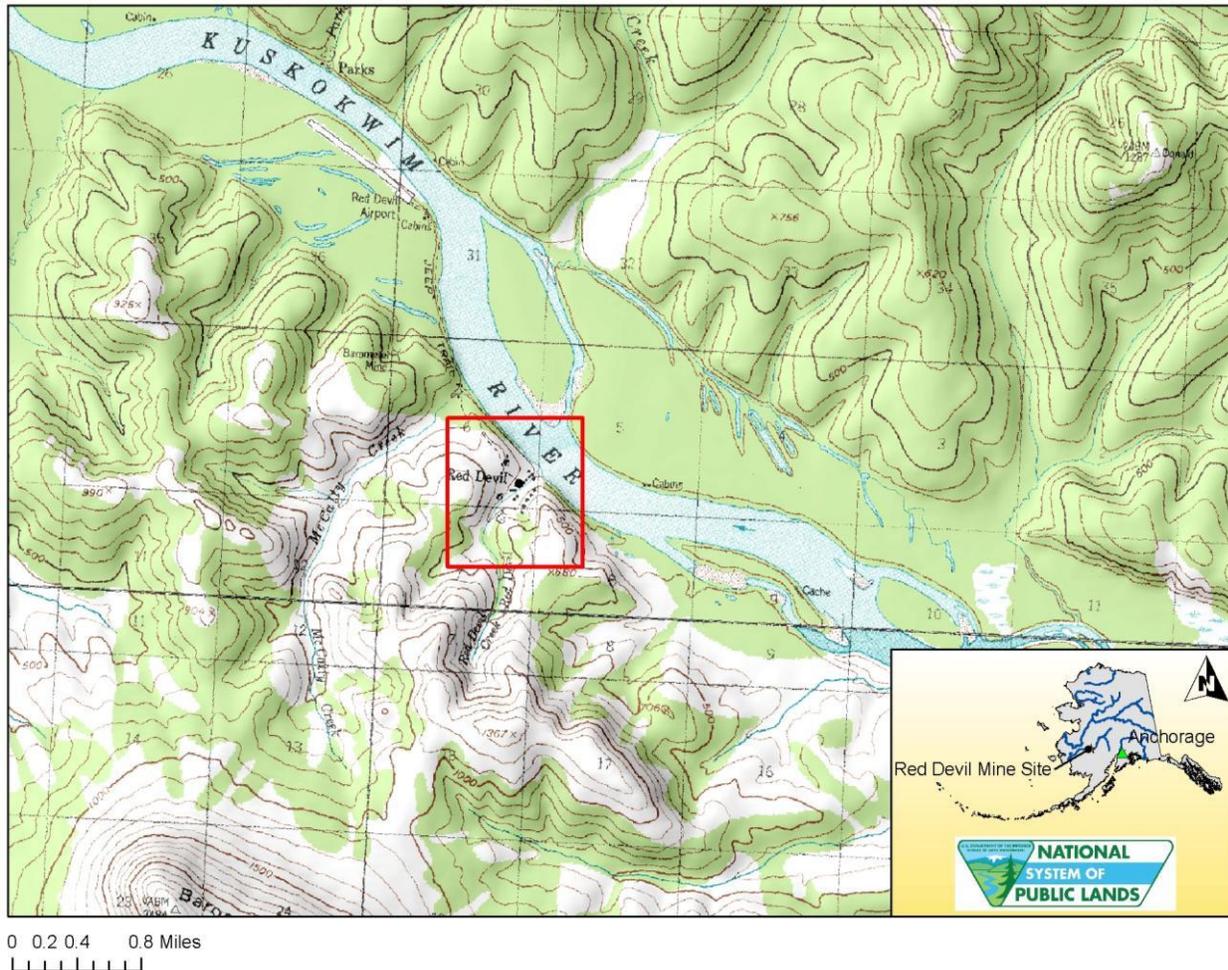
One of the largest abandoned mines in this section of the Kuskokwim River, the Red Devil Mine (RDM), is the site of an environmental investigation being conducted by the Bureau of Land Management (BLM). The data collected for this study provide a regional context for site specific data collected as part of the investigation. Aquatic macroinvertebrate and fish tissue methyl-mercury and total mercury concentrations will be incorporated into the human health and ecological risk assessments to be conducted as part of the environmental investigation. Establishing natural background conditions is critical to assessing the RDM's relative contribution to mercury and other metals concentrations in the aquatic ecosystem of the lower Kuskokwim River.

1.1 Background

The presence of mercury deposits along the Kuskokwim River is well known and several of the larger deposits, including Red Devil (see Figure 1), have been extensively mined. The presence of mercury in resident fish in the lower Kuskokwim has been the subject of study over the last 15 years. The Alaska Department of Fish and Game (ADF&G) (2007) reported from a 2001-2003 survey of two villages on the lower Kuskokwim River within the area near Red Devil Mine, that

households consumed 101-425 lbs of non-salmon fish on average annually. Non-salmon species typically are more susceptible to methyl-Hg (MeHg) accumulation because they reside entirely within the freshwater system, as such these species have a higher risk of bioaccumulation through the aquatic food web (Hanisch 1998, Wolfe et al. 1998). This MeHg accumulation is especially evident in predatory, piscivorous (fish-eating) fishes (Lepak et al. 2009a), since bioaccumulation in fish tends to rise with an increase in age and fish sizes (Johnels et al. 1967; Jewett et al. 2003).

Figure 1. Map of the Red Devil Mine Area



These aspects make subsistence species such as burbot (*Lota lota*) and Northern pike (*Esox lucius*) good candidates for this study, especially considering that these two species comprised 30-51% of the household fish consumption by pound in the sampled villages near the Red Devil Mine site from 2001-2003 (ADF&G 2007). Other high trophic level species such as adult Dolly Varden, arctic grayling, and sheefish are also harvested for subsistence and will good candidates for contaminant sampling. Additional sampling of lower trophic levels targeted at forage (prey) fish species and benthic aquatic macroinvertebrates will provide information on the relations between Hg bioaccumulation and food-web complexity. Wiener et al (2007) noted that top predators and 1-year old forage fish are the preferred indicators for monitoring trends

in Hg bioaccumulation in freshwater ecosystems. Several studies in western Alaska have examined contaminants in fish species within the last 20 years. Within the last decade, the USFWS completed extensive sampling of the lowermost segment of the Kuskokwim and Yukon Rivers to determine MeHg levels in northern pike (personal comm. A. Matz, USFWS 2010). Additionally, limited contaminant sampling of slimy sculpin in the Crooked Creek drainage, which joins the Kuskokwim River at the lowermost extent of the study area for this project, have occurred since 2004 (personal comm. E. Fleming, OtterTail Environmental 2010).

Jewett et al. (2003) summarized the results from 1987-2000 regarding Hg and MeHg in select fish species in western Alaska rivers. The authors concluded that “further studies are needed to determine the environmental and human health impacts associated with mercury concentrations in western Alaska, especially in the context of potentially increased consumption of resident fishes when anadromous salmon catches are reduced” which have steadily occurred since 1998 (e.g., McNair and Geiger 2001). Gray et al. (2000) conducted a study near the RDM site to evaluate the effects of abandoned Hg mines on fish and other aspects of the ecosystem. The authors noted that muscle samples of fish collected downstream from Hg mines, including RDM, on the Kuskokwim River contained as much as 420 and 620 ng/g Hg (wet wt. muscle) in sampled arctic grayling (*Thymallus arcticus*) and Dolly Varden (*Salvelinus malma*). These concentrations were several times higher than that in fish collected from regional baseline sites. Gray et al. (2000) concluded that elevated mercury concentrations in freshwater fish collected near abandoned Hg mines indicate that some biologically available Hg is taken up by fish; however the sample size was limited in respect to species more susceptible to MeHg bioaccumulation, such as northern pike (n=8).

1.2 Study Objectives

This study is designed to expand the sample size used by Gray et al. (2000) and more comprehensively examine Hg and MeHg in the Kuskokwim basin in proximity to the RDM (see Figure 2). The key elements of this study are severalfold. This study will:

- extend the sampling area beyond which was examined in previous contaminant efforts (e.g. Gray et al. 2000),
- focus on all trophic levels from benthic macroinvertebrates to upper level predators,
- target priority subsistence species
- provide data on tributary fish community composition, and;
- provide insight into tributary watershed health using metric analysis of benthic macroinvertebrates from sampled tributaries in the lower Kuskokwim River.

In keeping with previous work, concurrent sampling for contaminants, including Total Hg and MeHg, in surface waters and streambed sediments will also be completed. These data coupled with the fish tissue and macroinvertebrate contaminant data will yield information about the potential sources and relative bioavailability of Hg in the Kuskokwim and sampled tributaries.

The goal of this study is establish a baseline condition for the Kuskokwim River and tributaries between Stony River and Crooked Creek. The results will include several metals species, including Hg and MeHg, which may be bioaccumulating at various levels of the food web within the freshwater ecosystem. .

Specific objectives and associated tasks for this project are:

1. Estimate the levels of metal bioaccumulation within components of the aquatic food web in the lower Kuskokwim River.
 - a. Collect 144 whole fish samples from two-four upper trophic level species within the aquatic food web (i.e. a combination of pike, burbot, sheefish, Dolly Varden, and arctic grayling in priority order) during two distinct sampling events.
 - b. Collect 144 whole fish samples from two-four lower-mid trophic level species within the aquatic food web during two distinct sampling events.
 - c. Collect 24 composite benthic macroinvertebrate samples from sites located in eight tributaries in the Kuskokwim basin, including Red Devil creek.
 - d. Collect sediment and water samples at all tributary sampling locations. Analyze upper trophic level fish tissue and liver samples and low-mid trophic level fish tissue samples for the full suite of metals (Aluminum, Arsenic, Boron, Barium, Beryllium, Cadmium, Chromium, Copper, Iron, Magnesium, Manganese, Molybdenum, Nickel, Lead, Selenium, Strontium, Vanadium, and Zinc), and Total Hg.
 - e. Analyze a subset (approximately 10%) of the collected tissue and liver samples for MeHg to validate the >95% ratio of MeHg to Total Hg identified by Bloom et al. (1992), based on recommendations by Lepak et al. (2009b) and findings by Kannen et al. (2003).
 - f. Analyze benthic macroinvertebrate tissue samples for MeHg and Total Hg (if possible the full suite of metals would be analyzed).
 - g. Collect fork length (FL) and/or total length (TL) and weight of sampled fish species. All upper trophic level fish will be uniquely tagged and later processed to determine age for comparison with metals data.
 - h. If possible. lower level trophic species may be collected to determine age-length relationships.

In addition to the primary objective, secondary objectives and tasks will include:

2. Evaluating macroinvertebrate diversity within several watersheds using a variety of metrics to determine the level of variance between reference and test watersheds.
 - a. Collect at least eight composite samples per tributary for processing at the National Aquatic Monitoring Center for identification to genus/species and evaluation using a variety of metrics (see Maret et al. 2003, Clements et al. 2000).

- b. Document instream habitat conditions and water chemistry at sample sites.
3. Work with local residents in Stony River, Crooked Creek, and Sleetmute to identify relative locations of subsistence harvest areas on the Kuskokwim River within the project area.
 - a. Utilize the information in the formulation of subsequent sampling plans for burbot tissue collection and logistical planning for potential future telemetry efforts for burbot.

2.0 Sampling Locations

2.1 Biological Sampling

Upper trophic level fish samples will be collected from six distinct reaches of the Kuskokwim and major tributaries. Lower trophic level fish and macroinvertebrate samples will be collected from eight tributaries located between Crooked Creek and Sleetmute. The locations of the proposed sampling areas are shown in Figure 2.

2.2 Surface Water and Sediment Sampling

Surface water and sediment samples will be collected from eight tributaries and at two locations in the Kuskokwim River. Each surface water and sediment sample will be collected from the same location as macroinvertebrate samples collected from the eight tributaries, including Red Devil Creek. Kuskokwim River samples will be collected at previously established sampling points at Stony River (above the upper-most tributary) and at Crooked Creek (below the lower-most tributary). The locations of the tributaries to be sampled and the sampling locations on the Kuskokwim River are shown in Figure 3.

3.0 Sample Methods

3.1 Biological Sampling

All sampling will be conducted during summer (late June/July) and fall (September/October). Mainstem river and tributary sampling for fish, macroinvertebrates, and water/sediment would be completed within a 4-week period to ensure data comparison. Study design for fish and macroinvertebrate sampling for metals analysis will be based upon Scudder et al. (2008).

Fish sampling protocols would vary by the species being targeted. Burbot would be sampled using baited hoop traps (McCrimmon and Devitt 1954; Lawler 1963; Bernard et al. 1991) targeting fish within a diversity of older age classes: 3-5 yrs (300-450mm), 5-7 yrs (450-550mm), 7-10 yrs (550-650mm), and 10+ yrs (>650mm). Northern pike would be collected using a variety of techniques ranging from hook-and-line gear to gill nets (3/4") and would target similar age classes as outlined for burbot (i.e. 350-450mm, 450-500 mm, 550-700, and >700mm). Hoop traps would be tended at a frequency appropriate to remove captured and release non-target species or size classes. If gillnets were utilized they will be sampled regularly at 20 minute intervals to remove capture fish. If catch per unit effort is low, overnight net sets maybe used inside the mouth of sloughs. This technique may result in incidental capture of whitefish, which

would be utilized for hoop trap bait during or in future sampling events. Reduced capture efficiency within selected reaches for target species will result in the substitution of other upper level trophic species, such as Dolly Varden, arctic grayling, and sheefish, using similar age class lengths described above. All captured target fish within the sizes classes outlined above will be uniquely tagged using numeric locking tags, wrapped in foil, and placed in a portable freezer. Data sheets will be completed at each sampling location and include tagging information, fork length (mm), weight (g), and spatial location of the collection in NAD 83.

Forage fish will be collected using backpack electrofishing techniques within the lower segment (100 m) of the sampled tributaries. All sampled fish and macroinvertebrate for contaminant analysis will be uniquely identified within individual plastic resealable bags and placed on ice. Macroinvertebrate sampling for benthic diversity analysis would be collected based upon guidance provided by the BLM BugLab for Fixed Area Quantitative or Qualitative Invertebrate collection will take place upstream of the riffle(s) used for collection of macroinvertebrate samples for metals analysis. Samples will be labeled internally and externally and stored in ethanol within 1-quart collapsible containers. Data sheets will be completed at each sampling location for both the BLM BugLab and contaminant samples, which will include unique identification information, length (mm), weight (g), and spatial location of the collection in NAD 83.

3.2 Sediment Sampling

Stream sediment will be collected from surface-layer, bed-load alluvium at each macroinvertebrate/fish sampling site. Sample collection and preservation will follow accepted USEPA protocols (EPA 2001). Each single sediment sample will represent a separate composite. Sediment will be field sieved to <63 um in accordance with USGS protocol and spilt in the field into a mercury and trace element samples (Radke, 2005). Solid samples for trace element analysis are to be collected in triplicate, using amber glass vessels with Teflon lined lids, and then frozen until analyzed. Samples for Hg methylation and demethylation rate measurements also will be collected in amber glass vessels, but then refrigerated, not frozen. Prior to analysis, the stream-sediment samples would be air dried and pulverized to less than 100 mesh (0.15 mm).

3.3 Water Sampling

Unfiltered water samples for Hg and methyl-Hg analysis will be collected in triplicate. Water samples will be depth and width integrated samples collected according to USGS protocol (U.S. Geological Survey, variously dated) in teflon bottles pre-cleaned by boiling in concentrated nitric acid (HNO₃) for 48 hours. Within eight hours of collection, these water samples will be acidified with ultra-pure HCl using a final acid concentration of 0.5% (v/v). Unfiltered water samples collected for cation analysis will be collected in polypropylene bottles pre-cleaned in 10% HCl and these water samples are acidified on-site with ultra-pure HNO₃. Water samples for anion analysis are collected in clean, polypropylene bottles.

Discharge measurement will be made at each site where water samples are collected either by hand held flow meters or Doppler measurements.

4.0 Sample Analysis

4.1 Biological Samples

Laboratory sample processing and analysis will be completed by a contract laboratory and follow protocols outlined in EPA method 6020 and 7473 for metals and high-performance liquid chromatography (HPLC) coupled to inductively coupled plasma mass spectrometry (ICP-MS) technique for MeHg analysis.

The BLM BugLab would process the benthic diversity macroinvertebrate samples using the procedures recommended by the United States Geological Survey (Cuffney et al. 1993), which are described in greater detail in Vinson and Hawkins (1996).

4.2 Sediment and Water Samples

Concentrations of Hg and methyl-Hg will be determined using cold-vapor atomic fluorescence spectrometry (CVAFS). Measurement of total Hg follows protocols established in EPA Method 1631 (EPA 1996; 2002). Solid samples are digested using aqua regia (3 parts HCl: 1 part HNO₃) and the Hg ions in the digestate are reduced by acidic SnCl₂ to elemental Hg and purged from the sample with argon. The released Hg is then measured by CVAFS as outlined in EPA Method 1631. Methyl-Hg determinations follow EPA Method 1630 (Bloom 1989). During methyl-Hg analysis and sediment samples must be extracted into methylene chloride following digestion to avoid possible methylation artifact effects (Bloom et al. 1997). An ethylating agent is added to the extract to form a volatile methyl-ethylmercury derivative, and then purged onto graphitized carbon traps as a means of pre-concentration and interference removal. The samples are then isothermally chromatographed, pyrolytically broken down to elemental Hg and detected using CVAFS following the method of Bloom (1989).

Sediment and water samples will be sent to the USGS laboratory for determination of total Hg and methyl-Hg concentrations. Quality control for geochemical analyses, including Hg and methyl-Hg determinations, would be addressed with method blanks, blank spikes, matrix spikes, certified reference materials, and blind duplicates. Major and trace elements would be measured in sediment and water by inductively coupled plasma-mass spectrometry (ICP-MS) using techniques developed by Lamothe et al. (1999). Anions in water will be determined using ion chromatography. Water measurements such as temperature, conductivity, oxidation-reduction potential, dissolved oxygen, total dissolved solids, pH, and salinity will be made on-site with a Hydrolab instrument. Measurements will also be made on-site in water for concentrations of alkalinity, total Fe, reduced Fe (Fe²⁺), phosphate, ammonia, and sulfide using chemical test kits (manufactured by Chemetrics).

5.0 Data Analysis and Reporting

The intent of the biological sample analysis is to provide additional baseline data on the bioaccumulation of metals, including MeHg, in the lower Kuskokwim River and associated tributaries. Processed sample data by the contracted laboratory will be submitted for a third party quality assurance review before being considered complete.

Fish age analysis will be conducted on upper trophic level fish samples and summarized into a table by the ADF&G using the tag number as the unique sample identifier. If possible, some lower level trophic fish samples will be aged by ADF&G and summarized into a table to establish an age-length relationship for sampled species. BLM will integrate the metal analysis results from the contracted laboratory and fish age information from ADF&G into data spreadsheet. The spatial locations of sampled fish will also be included in the data spreadsheet. However, given the potential seasonal mobility of upper trophic level species within the Kuskokwim River, further interpretation of these data will likely be limited although the data may highlight areas requiring additional sampling in the future.

Results from the metals analysis of biological, sediment, and water samples collected in the tributaries will be summarized in a separate spreadsheet. These spreadsheets will serve as the basis for analysis by US DOI contaminants experts. Contaminant levels noted within fish and macroinvertebrates tissue, in addition to various macroinvertebrate diversity metrics and sediment/water quality data, would be compared across sites and to existing datasets in the region.

5.1 Sample Size

The number of fish and macroinvertebrate samples for metals analysis dictated by Scudder et al. (2008), the number of sampling areas being targeted, and environmental conditions. Table 1 below outlines the targeted sample sizes for each of the two sampling events.

Benthic diversity sampling would include the collection of one sample within each tributary targeted for metals analysis.

5.2 Schedules and Reports

A draft project report would be compiled by May 2011 and finalized by August 2011.

5.3 Responsibilities

Project Leader: Matthew Varner, Fisheries Program Lead, BLM – AK State Office
Duties: Coordinate sampling effort, contract oversight, lead tributary sampling of biological resources, compile data.

Table 1. Sample Size for Metals and Benthic Diversity Sampling

Macroinvertebrate Sampling (Per Round)	
8 tributaries (Target: 3 replicate composite samples)	24
Total Samples (MeHg + THg)	24
Top Predator Fish Sampling (Per Round)	
Reaches	6
Species (Target: N. Pike and Burbot)	2
# Samples per Reach	12
Total Number of Fish Sampled per round	144
Number of liver samples analyzed for Hg and other metals per round	144
Number of muscle samples analyzed for Hg and other metals per round	144
Number of liver samples analyzed for MeHg per round (10% of all fish sampled)	14
Number of muscle samples analyzed for MeHg per round (10% of all fish sampled)	14
Forage Fish Sampling (Each Round)	
Species (Target: S. Sculpin and other common spp)	2
# Samples per Tributary	24
Total Samples (8 Tributaries)	192
Total Number of Fish Sampled per round	192
Total Number of Whole Body Fish Sampled	192

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Figure 2. Map Depicting Fish Sampling Reaches and the Mouths of Targeted Tributary Watersheds

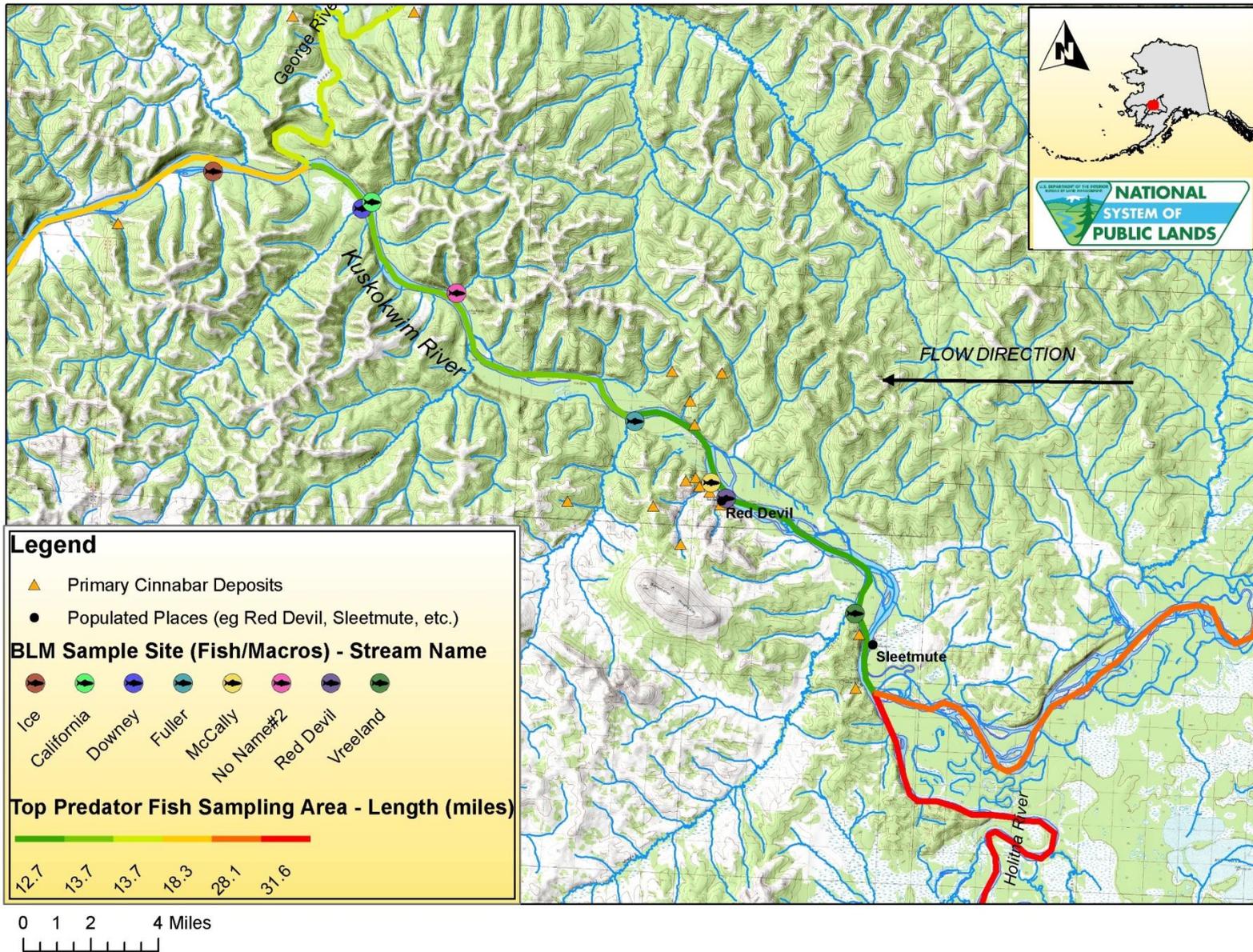
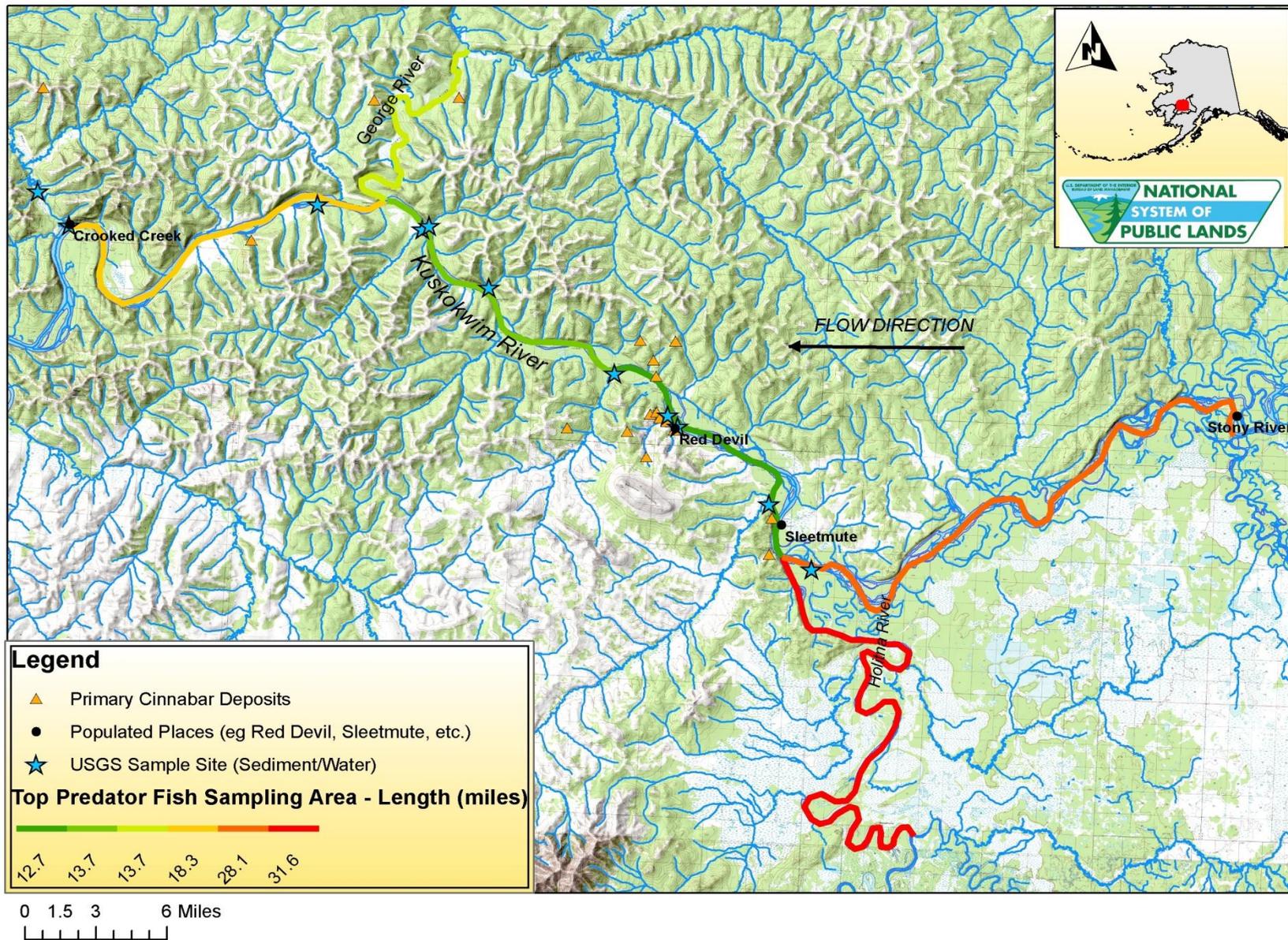


Figure 3. Map Depicting the Sediment/Water Sampling Locations by the USGS



Appendix 1. Field Forms

Macroinvertebrate Sampling Form (Metals)				
Stream Name:		Sample Date:		
Site ID:				
Time Range (24h), HHMM-HHMM				
Sample Type:				
Field Crew:				
Field Comments:				
Species Common Name:		Latin Name:		
Stream Habitat Sampled: Riffle Pool Run Margin				
Composite #	Sample time (24h)	# Individuals in Composite	Sample wet wt, field, g	Sample ID
1				
2				
3				

Fish and Macroinvertebrate Sampling Form (Metals)				
Stream Name:		Sample Dates (YYYYMMDD)		
Site ID:				
Time Range (24h), HHMM-HHMM				
Gear Types:				
Field Crew:				
Field Comments:				
Species Common Name:		Latin Name:		
Stream Habitat Sampled: Riffle Pool Run Margin				
Fish #	Sample time (24h)	Fork Length, total, mm	Fish wt, g	Sample ID
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				