

Third Screening Investigation of Water and Sediment Quality of Creeks in Ten Washington Mining Districts, with Emphasis on Metals

February 2004

Publication No. 04-03-005 *printed on recycled paper*

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Third Screening Investigation of Water and Sediment Quality of Creeks in Ten Washington Mining Districts, with Emphasis on Metals

by

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February 2004

Waterbody Numbers: see List of Waterbody Numbers

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This report was prepared by a licensed hydrogeologist and a licensed geologist. A signed and stamped copy of the report is available upon request.

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Table of Contents

List of Appendices

- A. Metals Criteria Formulas
- B. Results on Field Blanks for Water Samples
- C. Results on Field Replicates for Water Samples
- D. Results on Laboratory Splits for Metals in Water Samples
- E. Results on Laboratory Splits for General Chemistry
- F. Results on Field Replicates for Sediment Samples
- G. Results on Laboratory Splits for Sediment Samples
- H. Results on Field Measurements and General Chemistry for Water Samples
- I. Metals Concentrations in Water Samples
- J. Metals Concentrations in Sediment Samples
- K. Key for Water and Sediment Samples
- L. List of Minerals Referred to in this Report
- M. Glossary of Geologic and Mining Terms

List of Figures

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List of Tables

List of Tables (cont.)

Page

List of Tables (cont.)

List of Waterbody Numbers

- 1. Blewett District WA-45-1014 Peshastin Creek
- 2. Chiwawa District WA-45-2000 Chiwawa River
- 3. Wenatchee District WA-40-1000 Squilchuck Creek
- 4. Pend Oreille District/Sullivan Mill Area WA-62-1010 Pend Oreille River
- 5. Pend Oreille District/Metaline Mine Area WA-62-1010 Pend Oreille River
- 6. Chewelah District WA-59-1010 Colville River
- 7. Republic District WA-52-1010 San Poil River
- 8. Money Creek District WA-07-1210 Upper Skykomish River
- 9. Index District WA-07-1220 Lower Skykomish River
- 10. Mount Baker District WA-01-1197 Wells Creek

Abstract

This study was designed to characterize water and sediment quality in streams that drain ten metals mining districts. The districts were selected from a database prepared by Washington State Department of Natural Resources staff who identified the 60 largest inactive or abandoned metals mines in the state.

The study employed the EPA (1995) ultra clean and low-level sampling and analysis method for metals. General chemistry and field parameters were obtained concurrently with the metals and sediment samples.

Water samples were collected upstream and downstream of each district during fall 2002 for low-streamflow conditions, and during spring 2003 for high-streamflow conditions. Water samples also were obtained from a few mines that discharged to adjacent streams. Sediment samples were collected during low streamflow only. Results were compared upstream to downstream, seasonally, and to state surface water quality standards and sediment quality guidelines.

Four districts exceeded water quality standards for metals: arsenic in the Blewett District; zinc in the Pend Oreille District; copper, zinc, and cadmium in the Money Creek District; and copper in the Index District.

Seven districts exceeded sediment quality guidelines. Zinc, copper, cadmium, antimony, and arsenic sediment guidelines were most frequently exceeded, in that order.

The data were also used to continue development of a conceptual geochemical model that predicts water quality seasonality contrasts and investigation of a sulfate to total dissolved solids ratio for fingerprinting water quality impacts. The water quality analyses did not identify a consistent trend of seasonality in the data or definition of an absolute ratio useful for fingerprinting. In part, this may be due to a low level of spring recharge and runoff through the mine workings, tailings, and waste rock that are the sources for metals and oxidation products. The conceptual geochemical model predicts water quality impacts from a flushing mechanism that resolubilizes efflorescent minerals and discharges to adjacent streams.

Acknowledgements

The authors thank the following people for their contributions to this project:

- *Fritz Wolff and Mac McKay,* Washington State Department of Natural Resources, for preparing the DNR AML database and assistance in identifying candidate sampling sites.
- *Rich Stearns and Greg Graham*, U.S. Forest Service, for leading field trips to the Blewett and Chiwawa Districts.
- Washington State Department of Ecology staff:
	- o *Dean Momohara, Randy Knox, and Sally Cull* of the metals group, Ecology Manchester Environmental Laboratory, for analyzing samples.
	- o *Rick Frye, Dale Norton, and Wayne Peterson* for reviewing this report.
	- o *Ron Dixon*, Central Regional Office Water Resources Program, for preparing the figures in this report.
	- o *Joan LeTourneau* for formatting and editing the final report.

Summary

This study was a screening level investigation of ten metals mining districts in Washington State. The purpose of the study was to characterize water quality and sediment quality in some of the largest metals mining districts documented in Washington. This study was the third in a series of similar investigations of water and sediment quality in metals mining districts. Previous studies were conducted in 1997 (Raforth et al., 2000) and 2000-01 (Raforth et al., 2002).

Ten mining districts were selected from a database that has been prepared and maintained by the Washington State Department of Natural Resources (DNR). The database contains information on the geology, history, physical hazards, and geochemistry of the 60 largest mines in Washington. Data were obtained from DNR files, the U.S. Forest Service, U.S. Bureau of Land Management, former U.S. Bureau of Mines, and the Washington State Department of Ecology (Ecology). Staff from Ecology and DNR conducted the field sampling.

The ten districts included in this study were:

- 1. Blewett District, Kittitas County
- 2. Chiwawa District, Chelan County
- 3. Wenatchee District, Chelan County
- 4. Pend Oreille District/Sullivan Mill Area, Pend Oreille County
- 5. Pend Oreille District/Metaline Mine Area, Pend Oreille County
- 6. Chewelah District, Stevens County
- 7. Republic District, Ferry County
- 8. Money Creek District, King County
- 9. Index District, Snohomish County
- 10. Mount Baker District, Whatcom County

To adequately characterize water quality, the EPA (1995) ultra clean sampling method was used in conjunction with ultra low analysis by ICP/MS (inductively coupled plasma/mass spectrophotometry) and CVAA (cold vapor atomic absorption). Dissolved metals included in the characterization were arsenic, cadmium, copper, lead, and zinc. Aluminum, iron, and mercury were analyzed as total recoverable metals. General chemistry parameters were also analyzed: hardness, sulfate, total dissolved solids (TDS), total suspended solids (TSS), and turbidity. Conductivity, pH, and temperature were obtained as field measurements. Streamflows were estimated due to large errors associated with use of measuring devices such as the Marsh-McBirney flow meter in rocky streams.

Water quality sampling was conducted during October 2002 to characterize low streamflow conditions, and during May and June 2003 for high streamflow conditions. Sediment quality samples were collected only during low flow. At each site, an upstream and a downstream sample was collected. Discharges from a few mines also were sampled.

Results from the water quality samples were compared upstream to downstream, low flow to high flow, and to state surface water quality criteria for protection of aquatic life. Sediment sample results also were compared upstream to downstream and to recently recommended guidance for sediment quality values and cleanup standards levels (Michelson, 2003). The recommended guidance values have not been adopted by Ecology, but were considered appropriate for use in this screening level study.

Streams and mines in four districts failed to meet water quality criteria for one or more metals.

- 1. Mine water discharged from the Meteor Mine in the Blewett District did not meet the acute and chronic criteria for arsenic during both low-flow and high-flow sampling. The downstream sample in the adjacent creek was barely below the chronic criterion.
- 2. Discharge from the Metaline Mine in the Pend Oreille District contained zinc during low flow and high flow at concentrations that exceeded the acute and chronic criteria.
- 3. In the Money Creek District, downstream samples in Milwaukee Creek exceeded acute and chronic criteria for copper and zinc during both low flow and high flow. During high flow, copper and zinc concentrations also exceeded the acute and chronic criteria in the upstream sample. Cadmium exceeded the acute and chronic criteria in both the upstream and downstream samples for both low flow and high flow. Lead exceeded the chronic and acute and chronic criteria in the upstream sample during high flow.
- 4. Results from the Index District sampling showed that the Sunset Mine discharge and the downstream sample both exceeded acute and chronic criteria for copper during low flow and high flow.

Streams in three districts exceeded the guidelines for iron or aluminum:

- 1. Squilchuck Creek in the Wenatchee District (iron and aluminum)
- 2. Granite Creek in the Republic District (aluminum)
- 3. Wells Creek in the Mount Baker District (aluminum)

In addition to these exceedances of water quality criteria or guidelines, metals in some downstream samples also were documented to exceed the associated upstream concentrations by factors ranging from >2-fold to >10-fold, suggesting varying degrees of mine-related water quality impacts.

Sediment quality guidelines were exceeded in streams in seven districts in this study. Zinc, copper, cadmium, antimony, and arsenic constituted most of the sediment quality exceedances. Silver, chromium, nickel, iron, and lead also exceeded sediment guidelines.

- 1. Blewett District
- 2. Pend Oreille District/Sullivan Mill Area
- 3. Pend Oreille District/Metaline Mine Area
- 4. Chewelah District
- 5. Republic District
- 6. Money Creek District
- 7. Index District

In addition to characterizing water quality and sediment quality in metals mining districts, data were compared to a conceptual geochemical model that was developed from the data obtained in the two previous studies (Raforth et al., 2000, 2002). The model predicted that seasonal variations in water quality could be expected in metals mining districts and that a ratio of sulfate to total dissolved solids (sulfate:TDS) would be useful as a method of identifying water quality impacts due to discharges from mines, tailings, and waste rock. The basis for the model is the development of efflorescent mineralized salts in fractures and pores due to evaporation of fluids that contain dissolved metals and sulfate which are byproducts of the weathering of ore minerals and pyrite, a common mineral associated with most ore deposits.

During fall and winter, limited recharge through fractures and pores results in precipitation of the mineralized fluids as efflorescent salts. Then during spring and early summer runoff, the salts are dissolved and transported to a nearby stream or creek. The resolubilized metals and sulfate are similarly released, with the resultant increase in sulfate and metals concentrations in the receiving water. The most important factor is an adequate flux of recharge into the fractures and pores that will drive the resolubilization process and flush the metals and sulfate into the receiving water at levels that overcome the dilutive effect of the receiving water and result in exceedances of water quality criteria or significant concentration differences between upstream and downstream samples.

This study appears to have occurred under similar spring runoff conditions as the previous study (Raforth et al., 2002). Limited snowfall and subsequent recharge during the winter and spring of 2002-03 has apparently confounded the expectations from the model. Some seasonality was found in the data, and at a few sites the sulfate:TDS ratio appeared to have some application, but the results were not consistent or unambiguous.

Recommendations from this study include continued use of the EPA ultra low-level sampling and analysis method. Low detection limits afforded by this method provide water quality data at concentrations not previously attained. The dissolved metals included in sampling for this study, cadmium, copper, lead, arsenic, and zinc, should be carried forward for future studies. Total recoverable analyses for aluminum, iron, and mercury also should be included in future studies.

Water quality seasonality considerations in sampling design should be continued. Inconsistency in seasonality observed in recent data may be caused by lack of winter and spring precipitation which is necessary to drive changes in metals concentrations. For studies of this type, budgetary requirements dictate that project sampling must begin with the low-flow sampling event. If drought conditions occur during the following winter and spring, resulting in diminished spring runoff, there is no opportunity to adjust the schedule. A better approach for seasonal sampling projects would be to begin with the spring sampling event that can be assured to coincide with high-flow conditions followed by low-flow sampling later in the year. In fact, this was the approach for the first study (Raforth et al., 2000), which illustrated the role of seasonality in water quality results.

Another consideration would be to focus on districts that are in close proximity to each other or on a number of streams in several large districts. To accurately characterize seasonal water quality in the districts, it is desirable to optimize the timing of sampling to coincide as nearly as possible with high-flow conditions. If the mining districts selected for sampling are in different parts of the state and at different elevations, sampling each district at the appropriate time is difficult.

General chemistry analyses for sulfate and TDS should be continued in future studies. These parameters will allow continued calibration of the geochemical model, with the ultimate goal of determining an appropriate fingerprinting of discharges from mines using the sulfate:TDS ratio. DNR estimates that there are as many as 3,800 inactive and abandoned mines in the state. Although most of the mines do not have mine water discharges, a fingerprinting process is desirable. Turbidity and TSS analyses should be continued as they are useful indicators for field conditions and for explaining some of the metals results. Hardness is necessary for adjusting water quality criteria. Conductivity, pH, and temperature are easily obtained in the field and should be part of future studies. Flow should be directly measured where possible, and estimated using best professional judgment when necessary.

The results from this study should be used to direct additional sampling in the four districts where exceedances of water quality criteria were documented.

- The Meteor Mine in the Blewett District exceeded the water quality criterion for arsenic. The downstream sample nearly exceeded the criterion and far exceeded the background concentration. Additional sampling should be focused on other mines and streams in the district.
- In the Pend Oreille District, samples from two streams in this study and one stream in a previous study revealed exceedances of water quality criteria. Other metals showed more than 10-fold increases above background.
- The Pend Oreille District covers a large area with many streams and numerous mines that should be sampled in more detail. Milwaukee Creek in the Money Creek District exceeded water quality criteria for copper and zinc. Other mines and creeks in the district should be investigated and sampled as well.
- The Index District is another large mining district. Samples in the discharge from the Sunset Mine and downstream from the mine in Trout Creek exceeded the water quality criterion for copper. Other mines and streams in this district should be sampled.

For the most part, the above districts recommended for sampling based on water quality results also would be of interest based on sediment quality results. In addition to recommended water quality sampling in these four districts, one other district should be investigated based primarily on sediment quality.

• In the Republic District, only the EPA aluminum guideline was exceeded among the water quality criteria in Granite Creek. However, antimony, silver, and arsenic sediment quality guidelines were exceeded in the sediments in Granite Creek. The presence of tailings on the creek bank at a location in close proximity to the town of Republic is cause for further investigation.

Introduction

The objective of this study was to collect water quality and sediment quality data for selected metals, general chemistry, and field parameters at a screening level in streams that drain some of the metals mining districts in Washington State. For metals, the EPA (1995) ultra clean sampling and ultra low level analysis methods were used to achieve the low detection limits necessary to compare to standards. Data from this study are intended to be used as baseline information for permitting, total maximum daily load development, and biologists or others requiring information on water and sediment quality in the vicinity of metals mining districts. This study was the third in a series of cooperative investigations by Ecology and DNR of water and sediment quality in metals mining districts conducted by the same authors (Raforth et al., 2000, Raforth et al., 2002).

DNR estimates that there are over 3,800 inactive or abandoned metals mines in Washington (Wolff et al., 2001). The mines and districts included in this study were selected from a database developed and maintained by DNR. The database identifies the 60 largest metals mines from DNR files and information obtained from the U.S. Forest Service, U.S. Bureau of Land Management, the former U.S. Bureau of Mines, and Ecology.

Ten metals mining districts were selected from the DNR database:

The previous studies of water and sediment quality in metals mining districts contained recommendations to include certain metals and general chemistry parameters in future screening level studies. Those recommendations were followed in this study.

Parameters for the present study included:

^aMeasured as total recoverable metals

^bMeasured as dissolved metals

Water and sediment samples were collected as grabs upstream and downstream in each district. Water samples were collected in October 2002 to characterize low streamflow conditions and in May and June 2003 for high streamflow conditions. Sediment samples were collected only during low flow. Upstream water quality and sediment quality data were compared to downstream data to assess potential impacts from mining. The water quality data were also compared to state Water Quality Standards, Chapter 173-201A WAC. Sediment data were compared to sediment quality values and cleanup standards levels contained in recent guidance (Michelson, 2003).

Another aspect of this study was the collection of data to test a conceptual geochemical model developed from previous data. The model predicts that seasonality in water quality should result in higher concentrations of metals and sulfate released from mines, tailings, and waste rock during spring runoff. The other prediction is that the increase in sulfate concentration should allow calculation of a ratio of sulfate to total dissolved solids (sulfate:TDS) that would identify impacts from mining operations. The first study in this series suggested that an appropriate ratio would be 20%. Subsequent sampling has been less conclusive for identifying seasonality or for calculating such a ratio. It is believed that the first sampling project occurred during a favorable year of high spring runoff while subsequent studies have occurred during low runoff years.

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Water Quality Criteria

State surface water quality standards pertinent to the present study include standards for temperature, pH, turbidity, and metals (see Table 1). The metals standards are for acute (1-hour average not to be exceeded more than once every three years) and chronic (4-day average not to be exceeded more than once every three years) exposure. Field work for the present study was not conducted during periods when violations of the temperature standard would be likely to occur.

The acute and chronic standards for arsenic, cadmium, copper, lead, and zinc, as well as the acute standard for mercury, are for the dissolved fraction. The dissolved fraction of these metals was analyzed in the present study, except for mercury which was analyzed as total recoverable. The chronic mercury standard (0.012 ug/L) is for total recoverable. The acute standard for dissolved mercury (2.1 ug/L) is rarely exceeded in state surface waters and was not approached in the total recoverable analysis conducted for this study.

The standards for cadmium, copper, lead, and zinc are hardness dependent. Metals toxicity generally decreases with increasing hardness. For example, the cadmium acute and chronic criteria are 0.30 and 0.19 ug/L at 10 mg/L hardness, but increase to 3.7 and 1.0 ug/L at a hardness of 100 mg/L. Equations for calculating hardness-based metals criteria are provided in Appendix A.

There are no state standards for iron or aluminum. EPA has recommended that total recoverable iron and aluminum concentrations not exceed 1,000 ug/L and 750 ug/L, respectively, to protect freshwater aquatic life (EPA, 2002). The iron concentration is for chronic exposure (Criterion Continuous Concentration). The aluminum concentration is for acute exposure (Criterion Maximum Concentration) at pH values of 6.5 -9.0.¹

The Canadian Council of Ministers of the Environment (CCREM, 1986) has recommended substantially lower guidelines for both iron and aluminum. For iron, total concentrations should not exceed 300 ug/L. CCREM notes that the EPA iron criterion is too close to levels shown to adversely affect some aquatic species. For aluminum, total concentrations should not exceed 5 ug/L in waters with $pH < 6.5$, and should not exceed 100 ug/L for $pH > 6.5$.

Total suspended solids (TSS) also are not addressed in the state standards, except indirectly by way of the turbidity standard. The National Academy of Sciences (1973) considers the level of protection afforded aquatic communities to vary with TSS as follows:

• $\langle 25 \text{ mg/L} - \text{high} \rangle$

1

- 25 to 80 mg/L moderate
- 80 to 400 mg/L low
- $>400 \text{ mg/L}$ very low

¹ Previous reports in this series (Raforth et al., 2000, 2002) used an aluminum concentration of 87 ug/L (chronic) that was based on older EPA guidance.

Table 1. State Surface Water Quality Standards Pertinent to the Present Study

[see WAC 173-201A for complete standards]

 Zinc^{a} 114 104

^adissolved fraction

^btotal recoverable

Sediment Quality Criteria

There are no Washington State standards or EPA national criteria for chemical contaminants in freshwater sediments. Therefore, sediment criteria from other sources were used to assess the potential for metals-induced toxicity of sediments collected in streams below mining districts.

The Ecology Toxics Cleanup Program is currently considering using a draft set of sediment quality values (SQV) for freshwater sediments, described in Michelsen (2003). Michelsen calculated possible sediment quality standards (SQS) and cleanup screening levels (CSL) for zinc, lead, copper, chromium, nickel, cadmium, arsenic, silver, antimony, and mercury. Sediments with chemical concentrations equal to or less than the SQS values are expected to have no adverse effects on biological resources. The CSL is used to identify sediments of potential concern where further study, possibly leading to cleanup, may be warranted. The SQS and CSL values in the Michelsen report were provided to Ecology for discussion purposes only and have not been proposed or adopted by Ecology. Persaud et al. (1993), Ingersoll et al. (1996), and Cubbage et al. (1997) have proposed freshwater sediment criteria for iron, aluminum, and manganese, respectively. No sediment quality guidelines could be located for selenium, beryllium, or thallium.

The Michelsen (2003) and Cubbage et al. (1997) values are based on laboratory bioassays of freshwater sediments collected in Washington. The Persaud et al. (1993) and Ingersoll et al. (1996) criteria also include field data on effects to benthic invertebrate communities and are not specific to Washington. The SQVs from these various sources are summarized in Table $2²$

1

 2 Previous reports in this series (Raforth et al., 2000, 2002) relied solely on older sediment quality criteria developed by Cubbage et al. (1997) and MacDonald et al. (2000).

Metal	Sediment Quality Value		Source
		Type	
Iron	40,000	SEL	Persaud et al. (1993)
Aluminum	58,000	ERM	Ingersoll et al. (1996)
Manganese	1,800	LAEL	Cubbage et al., 1997)
Zinc	140/160	SQS / CSL	Michelsen (2003)
Lead	335/430	SQS / CSL	$^{\prime\prime}$
Copper	80/830	SQS / CSL	$^{\prime\prime}$
Chromium	95/100	SQS / CSL	$^{\prime\prime}$
Nickel	60/70	SQS / CSL	$^{\prime\prime}$
Cadmium	0.6 / 1.0	SQS / CSL	$^{\prime\prime}$
Arsenic	20/51	SQS / CSL	11
Silver	2.0 / 2.5	SQS / CSL	$^{\prime\prime}$
Antimony	0.4/0.6	SQS / CSL	$^{\prime\prime}$
Mercury	0.50 / 0.75	SQS / CSL	$^{\prime\prime}$
Selenium			
Beryllium			
Thallium			

Table 2. Guidelines on Metals in Freshwater Sediments (mg/Kg, dry)

SEL = severe effect level

ERM = effects range medium

SQS = sediment quality standard (draft recommendation, not proposed or adopted by Ecology)

 $CSL =$ cleanup screening level (draft recommendation, not proposed or adopted by Ecology)

Methods

Sampling and Field Analysis

All water samples were collected as simple grab samples. Water samples for metals analysis were collected directly into pre-cleaned 500 mL Teflon bottles. Samples for dissolved metals were vacuum-filtered in the field through a disposable 0.45 µm cellulose nitrate filter (#450-0045, type S). Non-talc, disposable gloves were worn during the filtering procedure. The filtrate was transferred to a clean Teflon bottle and preserved to pH <2 with 5 mL sub-boiled 1:1 nitric acid, carried in small Teflon vials, one per sample. Unfiltered water samples for total recoverable metals were preserved in the same manner. Sample containers and preservation for general water quality parameters are described in MEL (2003).

The Teflon bottles, acid vials, and filter units were pre-cleaned for low-level metals analysis using procedures described in Kammin et al. (1995). The bottles and vials were soaked in 1:1 nitric acid for 72 hours and rinsed with de-ionized (DI) water. The cleaned bottles were filled with DI water and placed in zip-lock bags. The filters were cleaned by allowing 1:1 nitric acid to gravity filter, then vacuum filtering 500 mL of DI water. The unit was taken apart, air-dried, reassembled, filter lids secured with tape, and placed in zip-lock bags.

pH, temperature, and conductivity were measured in the field with a YSI Model 63 meter. The meter was calibrated daily for pH.

Streamflow was estimated. If the channel configuration permitted, the methodology employed a stick or other floating object timed along a defined length of stream. For small streams a visual estimate or extrapolation of the time required to fill a one-liter sample bottle was used for flow since most of the streams were small, high gradient, and choked with cobbles and boulders.

A Garmin III Plus GPS Unit was used to determine latitude and longitude as well as elevations for the sampling stations. This information is found in Appendix K. Elevations and locations were verified in the field using USGS 7½ minute quadrangle maps. Elevations were also checked using a Thommen altimeter.

Sediment samples were composites of multiple grabs taken with stainless steel scoops and homogenized in the field in stainless steel beakers. Sampling equipment was cleaned by washing with Liquinox detergent and sequential rinses with tap water, dilute nitric acid, and DI water. The homogenate was split into glass jars, with Teflon lid liners, cleaned to EPA QA/QC specifications (EPA, 1990), or put in twist-lock bags for grain size.

All samples were double-bagged in polyethylene and placed on ice for transport to the Ecology Manchester Environmental Laboratory (MEL). Chain-of-custody was maintained.

Laboratory Analysis

Sample analysis was conducted at MEL. Water samples were analyzed directly for dissolved zinc, arsenic, copper, lead, and cadmium by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) following EPA method 200.8. Samples for hardness, total recoverable iron, and total recoverable aluminum were digested and/or analyzed following EPA method 200.7 (ICP). Hardness concentrations were calculated following Standard Methods SM2340B. Water samples for mercury were digested and analyzed by EPA methods 245.5 and 245.7, both Cold Vapor Atomic Absorption (CVAA). Analysis for general water quality parameters followed routine methods described in MEL (1999).

In sediment samples, metals other than mercury were digested with nitric and hydrochloric acids by EPA method 3050B and analyzed by ICP methods 200.7 and 200.8. Mercury was analyzed by EPA method 245.5. The mercury digestion employs aqua regia, potassium permanganate, and potassium persulfate.

Data Quality

MEL prepared written case narratives assessing the quality of the data collected for this project. These reviews include a description of analytical methods and an assessment of holding times, instrument calibration and calibration checks, method blanks, matrix spike recoveries, laboratory control samples, and laboratory duplicates. Few problems were encountered in analyzing samples for the present project, and the data are useable as qualified. These reviews and the complete MEL data reports are available from the first author on request.

The following certified/standard reference materials for metals were analyzed in addition to MEL's routine laboratory control samples: SLRS-4, River Water Reference Material for Trace Metals; NIST 1641, Mercury in Water; NIST 2709, San Joaquin Soil (mercury); and ERA 247, Metals in Sediment/Solids. Except for dissolved cadmium in SLRS-4, which was too low to be quantified, all recoveries were within acceptance limits.

Results from analysis of bottle and filter blanks prepared in the field during water sampling in October 2002 and May 2003 showed no evidence of significant metals contamination arising from sample collection, preservation, or handling (Appendix B).

Selected water and sediment samples were analyzed in duplicate to evaluate analytical precision (Appendix C). For general chemistry parameters and most metals analyses, results agreed within 20% or better. The results from duplicate analyses were averaged for use in this report.

Results

1. Blewett District, Chelan County

Geology³ and Historical Mining Operations and Practices

The first reported gold discovery of the Blewett mining district was by Mortimer Robertson in 1858 while gold panning. Placer mining occurred in the creeks until 1874 when Samuel Culver located a claim for gold on the gulch that now bears his name. The first lode claims were staked in 1874 by John Shafer (Patty, 1921).

At least 80 mines and prospects were located throughout Negro Creek, Culver Gulch, Peshastin Creek, and Culver Springs Creek (Huntting, 1943). The most significant mines in the district were the Culver Mine, Peshastin (Blewett) Mine, and the Pole Pick No. 1 Mine. A 20 stamp mill was established at Blewett Camp near the confluence of Culver Gulch and Peshastin Creek. Early milling was done by arrastre. When sufficient gold had accumulated in the trough an amalgam of gold and mercury was removed and separated using the retort method (Woodhouse et al., 1996). Production records from the various mines of the Blewett District are incomplete. However, according to Patty (1921) \$1,700,000 of gold was produced.

The host rocks of the deposit are part of the Ingalls complex which is disrupted Late Jurassic ophiolite complex. Igneous activity in the area includes the Late Cretaceous Mount Stuart batholith and intrusive rocks of early magmatic activity of the Cascades magmatic arc (Miller, 1985; Tabor et al., 1993). Most of the mineralization of Blewett Camp is in quartz and calcite veins cutting serpentinite of the Ingalls Complex. Some veins are in metasedimentary and metavolcanic rocks of the ophiolite complex (Derkey, 1990). Where veins cut gneissic rocks, the gangue is quartz with minor calcite. However, veins that cut serpentinite contain increasing amounts of calcite. The most productive veins are in Culver Gulch and trend $N75^{\circ}W$ (Huntting, 1943).

Commodities were gold, silver, mercury, and copper. Ore minerals are native gold, native copper, chalcopyrite, malachite, galena, stibnite, cinnabar, magnetite, hematite, and chromite. Non-ore minerals are pyrite, arsenopyrite, quartz, and calcite (Derkey, 1990).

Evaluation of Water Samples⁴

 \overline{a}

Three locations were sampled in this district during low streamflow and during high streamflow (Figure 2). The upstream samples were collected at Culver Springs, above all mining activity in the district, but in a different drainage than the other samples. The unnamed creek that drains the district was not flowing above all the known mines, and an unimpacted upstream stream sample

 3 Appendix L shows the composition of minerals referred to in this report.

Appendix M shows a glossary of geologic terms referred to in this report.

⁴ Complete field, general chemistry, and metals data for water are in Appendices H and I.

could not be taken. As a result, Culver Springs, which occurs in an adjacent drainage, was substituted as the upstream characterization site. Samples were obtained at the Meteor Mine, located about one quarter mile above the confluence of the unnamed creek in Culver Gulch with Peshastin Creek. The downstream samples were collected below the waste rock dump and other surface disturbances associated with the Meteor Mine.

For field parameters, pH increased from 7.07 at Culver Springs to 8.33 at the downstream sample during high flow (Table 3). For the high-flow sample, much of the runoff at the upstream site was due to melting snow which may have affected the pH value. During low flow, the upstream pH value was 8.40, which was higher than the downstream reading of 8.19. The pH measurements in the Meteor Mine drainage were slightly higher than the downstream readings during both high-flow and low-flow conditions. Conductivity measurements increased by more than 2-fold downstream for both high-flow and low-flow conditions. Conductivity of the Meteor Mine drainage was higher than the nearby downstream sample site during low flow, but lower than the downstream site during high flow. Both measurements exceeded the upstream sample site values.

Total dissolved solids (TDS) increased downstream by more than 2-fold in both the high-flow and low-flow samples and between the upstream sample and the Meteor Mine sample. TDS concentrations at all three sample sites were higher during low flow than during high flow. During high flow, sulfate concentration increased more than 10-fold from upstream to downstream and more than 20-fold from the upstream sample to the Meteor Mine. Sulfate concentrations during low flow were at least 2-fold higher than during high flow at each sample site.

Among metals, arsenic exceeded the water quality criterion in the discharge from the Meteor Mine. At low flow, arsenic concentrations increased from the nondetect value of $\langle 0.1 \text{ ug/L in} \rangle$ the upstream sample to 151 ug/L in the downstream sample and 479 ug/L in the Meteor Mine drainage (Table 4). Arsenic concentrations increased by a similar amount during high flow, with the Meteor Mine drainage concentration increasing to 554 ug/L and the downstream concentration at 126 ug/L. Both mine drainage samples substantially exceeded the chronic water quality criterion of 190 ug/L and the acute criterion of 360 ug/L. At the downstream site, arsenic concentrations were slightly below the water quality criteria.

Iron had a 2-fold increase between the upstream and downstream samples during high flow, but decreased downstream during low flow. The Meteor Mine drainage iron concentration increased from less than 25 ug/L at low flow to 135 ug/L at high flow. Dissolved copper concentrations increased during low flow by 3-fold from the upstream site to the downstream site and by 4-fold from the upstream site to the Meteor Mine drainage. Copper concentrations in the upstream and downstream samples were higher during high flow than low flow, but the Meteor Mine drainage showed a decrease.

Replicate water samples were collected in drainage from the Meteor Mine during high flow to provide estimates of the variability in the metals and general chemistry data (Table 5). There was little change in concentration between the two samples. These data were averaged for use in Tables 3 and 4.

Figure 2. Location of Water and Sediment Samples Collected in Culver Gulch, Blewett District.

Table 3. Field Measurements and General Chemistry Results for Blewett District Water Samples Collected September 2002 and May 2003

Detections highlighted in **BOLD**

 $J =$ estimated value

 $U = not detected at or above the reported value$

 UJ = not detected at or above the reported estimated value

Table 4. Metals Concentrations in Blewett District Water Samples Collected September 2002 and May 2003 (ug/L)

Metals detections highlighted in **BOLD**

*= exceeds water quality standard or guideline

 $U = not detected at or above the reported value$

Location		Meteor Mine	
Date	06-May-03		
Sample No.	194021	194022	RPD
TSS (mg/L)	1U	4	$>120\%$
TDS (mg/L)	251	250	0%
Sulfate (mg/L)	27.4	27.2	${<}1\%$
Turbidity (mg/L)	0.5J	0.5J	0%
Iron (ug/L)	130	140	7%
Aluminum (ug/L)	20U	20U	
Zinc (ug/L)	3.3	2.7	20%
Copper (ug/L)	0.544	0.526	3%
Arsenic (ug/L)	551	556	1%
Cadmium (ug/L)	0.020U	0.020U	
Lead (ug/L)	0.020U	0.020U	
Mercury (ug/L)	0.0020U	0.0020U	
Hardness (mg/L)	219	218	0%

Table 5. Results from Field Replicates on Blewett District Water Samples

Detections highlighted in **BOLD**

RPD = relative percent difference (range as percent of duplicate mean)

 $J =$ estimated value

 $U = not detected at or above the reported value$

Evaluation of Sediment Samples⁵

Recommended sediment quality standards (SQS) and/or cleanup screening levels (CSL) were exceeded for chromium, copper, nickel, and arsenic (Table 6). Chromium concentrations of 264 mg/Kg in the upstream sample and 389 mg/Kg in the downstream sample both exceeded the SQS and CSL of 95 and 100 mg/Kg respectively. Copper increased downstream from 34.6 mg/Kg to 112 mg/Kg, which exceeded the SQS of 80 mg/Kg but not the CSL of 830 mg/Kg. Nickel concentrations increased from 404 mg/Kg in the upstream sample to 450 mg/Kg, both of which exceeded the SQS of 60 mg/Kg and the CSL of 70 mg/Kg. Arsenic in sediments paralleled the increase noted in water, with the upstream sample concentration of 0.57 mg/Kg increasing to 468 mg/Kg in the downstream sample, which far exceeded the SQS of 20 mg/Kg and the CSL of 51 mg/Kg. The concentration of iron increased downstream to 42100 mg/Kg which slightly exceeded the recommended severe effects level of 40000 mg/Kg. The concentration of mercury increased more than 12-fold downstream, but did not exceed the recommended standard. A sediment sample was not collected in the Meteor Mine drainage.

 $* =$ exceeds sediment quality guideline

 $U =$ not detected at or above the reported value

 $J =$ estimated value

 \overline{a}

⁵ Complete metals data for sediment are in Appendix J.

2. Chiwawa District, Chelan County

Geology and Historical Mining Operations and Practices

The discovery of mineralization in the Chiwawa mining district occurred in the 1890s. The eventual owner of the claims was the Royal Development Company in 1908. The Red Mountain Mine was alternatively known as the Royal or the Trinity. The mine closed in 1937 after producing about 15,000 tons of ore (Huntting, 1956). Assays reported by Huntting (1943) show a "trace to 1.93% copper, 0.61 to 5.38 oz silver, and a little gold per ton".

Sulfide mineralization (principally pyrrhotite and chalcopyrite) is most extensive in a brecciated zone between the pre-Tertiary Swakane Biotite Gneiss and an unnamed Tertiary labradorite granodiorite intrusion (Cater and Crowder, 1967). Traces of the tungsten mineral scheelite occur as disseminated grains and veinlets (Culver and Broughton, 1945). A 250 ft. wide breccia zone lying between the contact of the biotite gneiss and the labradorite granodiorite is the principal structural feature associated with mineralization (Culver and Broughton, 1945). The mineralized zone may be hosted by a breccia pipe associated with the Cloudy Pass pluton (Church and Stotelmeyer, 1984).

Commodities were copper, silver, gold, zinc, lead, and tungsten. Ore minerals are chalcopyrite, sphalerite, galena, and scheelite. Non-ore minerals are pyrrhotite, pyrite, arsenopyrite, chlorite, quartz, calcite, biotite, and sericite (Derkey et al., 1990).

Evaluation of Water Samples

Water and sediment samples were collected near the Trinity Mine in Phelps Creek above the confluence with the Chiwawa River, representing the downstream sample site (Figure 3). Abandoned mines are present at the top of the Phelps Creek watershed; as a result, an unimpacted upstream sample site was not available in Phelps Creek. Samples to characterize upstream water and sediment quality were collected in the Chiwawa River above the confluence with Phelps Creek and upstream of the Trinity townsite and mill tailings.

The field parameters pH and conductivity decreased from low-flow to high-flow conditions at both sample sites (Table 7). During low flow, pH was lower in Phelps Creek than in the Chiwawa River, but during high flow, the reverse was observed. Conductivity was lower in the Chiwawa River than in Phelps Creek at high flow and at low flow. Hardness, TDS, and sulfate had higher concentrations in Phelps Creek than in the Chiwawa River during both low-flow and high-flow conditions. High-flow concentrations were lower than low-flow concentrations for these parameters.

Figure 3. Location of Water and Sediment Samples Collected in Phelps Creek and Chiwawa River, Chiwawa District.
		Flow (cfs)		Temp. $(^{\circ}C)$	pH (units)		Conductivity (uS/cm)		Hardness (mg/L)	
	Low	High	Low	High	Low	High	Low	High	Low	High
Sample Location	Flow	Flow	Flow	Flow	Flow	Flow	Flow	Flow	Flow	Flow
Chiwawa River	100J	300J	5.4	6.3	8.11	7.12	26	15	9.61	5.66
Phelps Creek	6.5J	20J	6.4	6.6	7.88	7.20	59	30	25.7	12.6
		TDS (mg/L)		TSS (mg/L)	Turbidity (NTU)		Sulfate (mg/L)			
	Low	High	Low	High	Low	High	Low	High		
Sample Location	Flow	Flow	Flow	Flow	Flow	Flow	Flow	Flow		
Chiwawa River	24J	20	1 _{UJ}	5	1.2J	3.8	2.46	1.2		
Phelps Creek	44J	28	1 _{UJ}	3	0.5UJ	0.8	5.14	$2.2\,$		

Table 7. Field Measurements and General Chemistry Results for Chiwawa District Water Samples Collected September 2002 and June 2003

Detections highlighted in **BOLD**

 $J =$ estimated value

 UJ = not detected at or above the reported estimated value

The aluminum concentration of 230 ug/L in the Chiwawa River during high flow exceeded the Canadian water quality guideline of 100 ug/L but not the EPA guideline of 750 ug/L. The concentrations of aluminum, iron, and copper were lower in Phelps Creek than in the Chiwawa River during both high-flow and low-flow conditions. High-flow concentrations of these metals were higher than the low-flow concentrations. High-flow and low-flow arsenic concentrations increased 3-fold or more from the background in the Chiwawa River to Phelps Creek. Low-flow arsenic concentrations were higher than high-flow concentrations. Zinc, cadmium, lead, and mercury were not detected in either the high-flow or low-flow samples from both Phelps Creek and the Chiwawa River.

Table 8. Metals Concentrations in Chiwawa District Water Samples Collected September 2002 and June 2003 (ug/L)

Metals detections highlighted in **BOLD**

None of the recommended sediment quality standards or cleanup screening levels were exceeded in the Chiwawa River or Phelps Creek (Table 9). Nearly 2-fold increases in the zinc and lead concentrations were noted. Aluminum, cadmium, chromium, copper, iron, manganese, nickel, arsenic, lead, and mercury were present in the samples.

Metals detections highlighted in **BOLD**

 $U = not detected at or above the reported value$

 UJ = not detected at or above the reported estimated value

 $J =$ estimated value

3. Wenatchee District, Chelan County

Geology and Historical Mining Operations and Practices

Original discovery claims in the Wenatchee area were by Morgan Carkeek in 1885 in Squilchuck Canyon. Carkeek's discovery became known as the Gold King, Golden King, Wenatchee, and Squilchuck (Derkey, 1995). Sporadic production occurred prior to 1949 and resulted in 26,600 tons of ore of unknown grade or gold recovery (Huntting, 1956). In 1949, the Lovitt Mining Co. gained control of the property and developed a mine known as the Lovitt or L-D Mine. From 1949 until 1967, Lovitt mined 1,036,572 tons of ore and recovered 410,482 oz of gold and 625,849 oz of silver (Patton and Cheney, 1971). The Cannon Mine, located in Dry Gulch approximately one mile to the northeast of the Lovitt Mine, produced 1,198,546 oz of gold and 1,987,105 oz of silver (Cameron, 1994).

The mines in the Wenatchee area are thought to be hosted by the Middle to late Eocene Chumstick Formation and Paleocene Swauk Formations. Coarse-grained arkose with silty partings is the dominant lithology, interbedded with carbonaceous mudstone. Conglomerates, volcanic flows, and tuffs are also present (Cameron, 1994). The Lovitt Mine is in the Chiwakum graben, a north-northwest trending right lateral strike slip graben bounded by the Entiat fault on the east and Leavenworth fault zone on the west (Ott et al., 1986). Associated igneous rocks are intrusive Eocene rhyodacite porphyry of the Wenatchee dome and the Rooster Comb and the Saddle Rock andesite (Gresens, 1983).

Mineralization occurs in host rocks in areas affected by wall rock silicification. Mineralization consists of vein, stockwork, and disseminated gold and silver. Two sets of fractures control vein mineralization. Ore minerals are electrum, native gold, pyrargyrite, naumannite, acanthite, aguilarite, chalcopyrite, stibnite, sphalerite, galena, and hessite. Non-ore minerals are pyrite, arsenopyrite, marcasite, quartz, chalcedony, adularia, calcite, and siderite (Derkey et al., 1990).

Evaluation of Water Samples

Water and sediment samples in this portion of the Wenatchee District were obtained in Squilchuck Creek above and below tailings deposited in the creek bed. The downstream sample site was located immediately below the tailings impoundment while the upstream samples were located about one mile upstream of the tailings (Figure 4).

For field parameters, pH and conductivity increased slightly in the downstream direction and were also higher in low-flow conditions than during high-flow conditions (Table 10). Hardness, TDS, and sulfate also increased downstream (Table 10). The values were higher during low flow than during high flow. Suspended solids and turbidity concentrations below the tailings were less than upstream concentrations for both low-flow and high-flow conditions. The upstream suspended solids and turbidity values were the highest obtained in any samples during this project.

Figure 4. Location of Water and Sediment Samples Collected in Squilchuck Creek, Wenatchee District.

Table 10. Field Measurements and General Chemistry Results for Wenatchee District Water Samples Collected October 2002 and May 2003

Detections highlighted in **BOLD**

 $J =$ estimated value

Aluminum and iron concentrations exceeded EPA guidance values of 750 ug/L and 1000 ug/L, respectively, at the upstream and downstream sample sites during both high flow and low flow (Table 11) and were the highest concentrations obtained during this study. Concentrations were higher during high flow, and were lower below the tailings than in the upstream samples. Copper and lead concentrations were about the same comparing low flow to high flow, and increased slightly downstream. Mercury concentrations were slightly elevated in high flow compared to low flow, but were lower downstream of the tailings than above the tailings. Cadmium and zinc were the only metals not detected during either low flow or high flow.

Table 11. Metals Concentrations in Wenatchee District Water Samples Collected October 2002 and May 2003 (µg/L)

	Aluminum (total recoverable)		Iron (total recoverable)		Copper (dissolved)		Zinc (dissolved)	
Sample Location	Low Flow	High Flow	Low Flow	High Flow	Low Flow	High Flow	Low Flow	High Flow
Squilchuck Creek Up	1050*	2020*	1310*	1860*	0.35	0.43	1U	1U
Squilchuck Creek Down	1040*	$1210*$	1363*	$1420*$	0.53	0.48	1U	1U
		Arsenic			Lead			
			Cadmium (dissolved)					Mercury
		(dissolved)				(dissolved)		(total recoverable)
Sample Location	Low Flow	High Flow	Low Flow	High Flow	Low Flow	High Flow	Low Flow	High Flow
Squilchuck Creek Up	0.62	0.36	0.02U	0.02U	0.02U	0.021	0.0038	0.0045

Metals detections highlighted in **BOLD**

 $* =$ exceeds water quality standard or guideline

Replicate water samples were collected in Squilchuck Creek at the downstream sample site during low-flow conditions to provide estimates of the general chemistry and metals data (Table 12). Iron and aluminum showed the greatest variability. The values in Tables 10 and 11 reflect averaged concentrations.

Location	Squilchuck Creek Downstream					
Date						
Sample No.	408310	408312	RPD			
TSS (mg/L)	26J	25J	4%			
TDS (mg/L)	210J	210J	0%			
Sulfate (mg/L)	8.53	8.58	1%			
Turbidity (mg/L)	14.J	13J	7%			
Iron $(\mu g/L)$	1030	1520	38%			
Aluminum (ug/L)	699	1190	52%			
Zinc (ug/L)	1U	1U				
Copper (ug/L)	0.52	0.53	2%			
Arsenic (ug/L)	0.86	0.87	1%			
Cadmium (ug/L)	0.02U	0.02U				
Lead $\left(\frac{u g}{L}\right)$	0.021	0.02U	$>5\%$			
Mercury (ug/L)	0.0036	0.0032	12%			
Hardness (mg/L)	130	130	0%			

Table 12. Results from Field Replicates on Water Samples Wenatchee District Collected October 2002

Metals detections highlighted in **BOLD**

RPD = relative percent difference (range as percent of duplicate mean)

 $* =$ exceeds water quality standard or guideline

None of the recommended sediment quality standards or cleanup screening levels were exceeded in upstream or downstream samples on Squilchuck Creek (Table 13). Aluminum, beryllium, chromium, copper, iron, manganese, nickel, zinc, arsenic, lead, and mercury were detected in the samples. The concentrations of these metals increased slightly downstream.

Metals detections highlighted in **BOLD**

 $U = Not detected at or above the reported value$

 $J =$ estimated value

Replicate sediment samples collected in Squilchuck Creek in October 2002 showed similar results for all metals (Table 14). These data were averaged for use in Table 13.

Location	Squilchuck Creek Downstream							
Date		01 -Oct-02						
Sample No.	408440	408442	RPD					
Antimony	0.2U	0.2U						
Arsenic	1.67	1.28	26%					
Chromium	14.7	10.6	32%					
Cadmium	0.1U	0.1U						
Silver	0.1U	0.1U						
Selenium	$0.1\mathrm{U}$	0.1U						
Zinc	35.6	34.9	2%					
Copper	5.74	5.37	7%					
Beryllium	0.27	0.24	12%					
Lead	4.51	4.30	5%					
Thallium	0.1U	0.1U						
Aluminum	8190	9270	12%					
Iron	14300	14300	0%					
Manganese	243	209	15%					
Mercury	0.0095J	0.0068J	33%					

Table 14. Results from Field Replicates on Sediment Samples in Wenatchee District Collected October 2002 (mg/Kg, dry)

Metals detections highlighted in **BOLD**

RPD = relative percent difference (range as percent of duplicate mean)

 $U =$ not detected at or above the reported value

 $J =$ estimated value

4. Pend Oreille District/Sullivan Mill Area, Pend Oreille County

Geology and Historical Mining Operations and Practices

Many mine workings are scattered throughout the Metaline District. One of those included in this study is the Sullivan and Josephine mines and associated mill and tailings along the South Fork of Flume Creek. Mining began at the Sullivan in 1926 and lasted about one year (Huntting, 1956). The glory holes are less than 200 ft in diameter and are 75 ft deep. Some tunneling has been done beneath the Sullivan gloryhole. Stratigraphically the mined horizon lies within the upper 50-200 ft of the Metaline Limestone. The principal workings on the east side of the Pend Oreille River are not connected to these mines.

The tectonic setting for the district is a sequence of Lower Paleozoic shallow marine sandstone, carbonate, and shales (miogeosynclinal rocks). All of the lead zinc deposits of the district are considered Mississippi Valley type found in Middle Cambrian to Middle Ordovician dolomitic limestones (Huntting, 1956).

Commodities were zinc, lead, and silver. Ore minerals are sphalerite and galena. Non-ore minerals are pyrite, dolomite, and calcite (Derkey, et al., 1990).

Evaluation of Water Samples

Water and sediment samples were collected in Flume Creek below the Sullivan Mill tailings and about one-half mile upstream of the tailings (Figure 5). Both high streamflow and low streamflow samples were obtained for water quality. Sediment samples were collected only during low flow. Iron staining associated with seeps was noted along the creek bank below the tailings during low flow. At high flow these seeps were submerged by runoff in Flume Creek.

Measurements of pH in Flume Creek showed little contrast between the upstream and downstream sample sites during both low-flow and high-flow conditions (Table 15). Both pH and conductivity measurements were higher during low flow than during high flow. Conductivity and pH measurements were made in four seeps below the tailings on the bank of Flume Creek near the downstream sample site. Conductivity ranged from 502 uS/cm to 579 uS/cm which contrasts with the downstream conductivity measurement in Flume Creek of 133 uS/cm. The pH in the seeps ranged from 7.74 to 8.07 compared to the pH in Flume Creek of 8.39. The concentrations of general chemistry parameters – hardness, TDS, and sulfate – followed the same pattern of little contrast between upstream and downstream samples and higher concentrations during low flow than during high flow.

Figure 5**.** Location of Water and Sediment Samples Collected in Flume Creek, Pend Oreille District**.**

Table 15. Field Measurements and General Chemistry Results for Pend Oreille District/ Sullivan Mill Area Water Samples Collected October 2002 and May 2003

Detections highlighted in **BOLD**

 $J =$ estimated value

 $U = not detected at or above the reported value$

 UJ = not detected at or above the reported estimated value

The concentration of aluminum increased downstream by more than 4-fold at low flow and 2-fold at high flow (Table 16). The low-flow concentration exceeded the Canadian guidance of 100 ug/L but not the EPA guidance of 750 ug/L. Iron and copper were the only metals detected during high flow in the upstream sample. Iron increased concentration by more than 2-fold downstream during low flow, and exceeded the Canadian guideline of 300 ug/L but did not exceed the EPA guidance of 1000 ug/L. Copper concentration stayed about the same between the upstream and downstream sites during high flow and increased downstream by about 2-fold during low flow. Zinc increased downstream more than 12-fold during low flow and nearly 40-fold during high flow. Arsenic increased 2-fold downstream during low flow but only increased slightly during high flow. Cadmium increased by about 4-fold during high flow but increased only slightly during low flow.

Replicate water samples were collected at the downstream sample site in Flume Creek during low-flow conditions (Table 17). Iron, aluminum, and copper exhibited the greatest variability, approaching or exceeding 100% Relative Percent Difference (RPD). Iron and aluminum RPD variability can be explained by the fact that those analyses are not filtered (total recoverable). The variability in the concentration of dissolved copper cannot be explained in the same manner. The concentrations in Table 16 reflect the average of the original sample and the replicate.

Table 16. Metals Concentrations in Pend Oreille District/Sullivan Mill Area Water Samples Collected October 2002 and May 2003 (μ g/L)

Metals detections highlighted in **BOLD**

 $U =$ not detected at or above the reported value

Metals detections highlighted in **BOLD**

RPD = relative percent difference (range as percent of duplicate mean)

 UJ = not detected at or above the reported estimated value

Cadmium, iron, and zinc exceeded the recommended sediment quality standards (SQS) and cleanup screening levels (CSL) (Table 18). Cadmium concentrations of 1.05 mg/Kg in the upstream sample and 1.53 mg/Kg in the downstream sample exceeded the SQS of 0.6 mg/Kg and the CSL of 1.0 mg/Kg. The upstream iron concentration of 44,100 mg/Kg exceeded the proposed severe effect level of 40,000 mg/Kg, but the downstream sample did not exceed the proposed value. The zinc concentration of 347 mg/Kg in the upstream sample and 478 mg/Kg in the downstream sample both exceeded the SQS of 140 mg/Kg and the CSL of 160 mg/Kg. The downstream concentration of mercury increased 6-fold to 0.060 mg/Kg but was well below the SQS of 0.5 mg/Kg and the CSL of 0.75 mg/Kg.

Table 18. Metal Concentrations in Sediment Samples Pend Oreille District/Sullivan Mill Sediment Samples Collected October 2002 (mg/Kg, dry)

Metals detections highlighted in **BOLD**

 $* =$ exceeds sediment quality guideline

A replicate sediment sample was obtained during low-flow conditions at the downstream sample location (Table 19). Cadmium, manganese, and zinc exhibited the greatest variability in the sediments. Table 18 contains averaged concentrations.

Metals detections highlighted in **BOLD**

 $RPD =$ relative percent difference (range as percent of duplicate mean)

5. Pend Oreille District/Metaline Mine Area, Pend Oreille County

Geology and Historical Mining Operations and Practices

The presence of lead deposits in the Metaline District was known as early as 1869, but no attempt at mining was made until about 1886 (Dings and Whitebread, 1965). The Metaline Mine was the name given to an adit for mining the combined ore bodies of the Bella May, Blue Bucket, and West contact deposits (Huntting, 1956). The Metaline is the third largest producer (410,724 tons of ore) in the district, behind the Pend Oreille Mine (5,451,328 tons of ore) and Grandview Mine (2,347,974 tons of ore) (Huntting, 1956).

The workings of the Metaline Mine have about 12,000 feet of extent and are connected to a haulage adit that is 6,600 feet long (Hunting, 1956). The mine workings expose hundreds of faults that range in displacement from a few inches to 1,000 feet or more. Four major faults are: the Metaline Thrust, the Blue Bucket fault which strikes NE and dips 60° NW with a throw of 700 ft, the Bella May fault which strikes NE and dips 65° SE and has a dip slip of 1,075 feet, and the West Contact fault which strikes north and dips $30-50^{\circ}$ W with a throw of 20 feet (Dings and Whitebread, 1965).

The lead zinc deposits are considered Mississippi Valley type found in Middle Cambrian to Middle Ordovician dolomitic limestones (Huntting, 1956) and are located in the Josephine Horizon of the Metaline Formation (Park and Cannon, 1943; Dings and Whitebread, 1965; Mills, 1977). The tectonic setting for the district is a sequence of Lower Paleozoic shallow marine sandstone, carbonate, and shales (miogeoclinal rocks).

Commodities were zinc, lead, and silver. Ore minerals are sphalerite, galena, and uranium. Non-ore minerals are pyrite, marcasite, silicified limestone, and dolomite (Derkey et al., 1990).

Evaluation of Water Samples

Samples for water and sediment quality were collected in Linton Creek as an upstream sample site to compare to the drainage from the Metaline Mine as it discharges into the Pend Oreille River near the town of Metaline (Figure 5). Water quality samples were collected during high flow and low flow, while sediments were sampled only during low-flow conditions.

Among field parameters, pH increased from Linton Creek to the Metaline Mine during low flow, but decreased during high flow (Table 20). There was an overall decrease in pH from low flow to high flow. Conductivity increased slightly from Linton Creek to the Metaline Mine during low flow and increased over 3-fold during high flow. For general chemistry parameters, hardness increased over 3-fold from Linton Creek to the Metaline Mine during both low flow and high flow. There was little change in hardness between low flow and high flow. There was a more than 4-fold increase in TDS concentration from Linton Creek compared to the Metaline

Mine discharge during both low flow and high flow, and more than a 20-fold increase in sulfate concentration. Concentrations of both TDS and sulfate decreased slightly from low flow to high flow.

Table 20. Field Measurements and General Chemistry Results for Pend Oreille District/ Metaline Mine Area Water Samples Collected October 2000 and April 2001

Detections highlighted in **BOLD**

 $J =$ estimated value

 $U =$ not detected at or above the reported value

 UJ = not detected at or above the reported estimated value

Copper concentration increased nearly 7-fold during low flow and nearly 5-fold during high flow from Linton Creek to the Metaline Mine discharge (Table 21). Copper concentration decreased slightly from low flow to high flow at the Metaline Mine, but remained the same in Linton Creek. During low flow, zinc concentration increased from 2.0 ug/L in Linton Creek to 1180 ug/L in the Metaline Mine which exceeded the hardness adjusted acute water quality criterion of 267 ug/L and the chronic criterion of 244 ug/L. During high flow, zinc increased from 2.3 ug/L to 1580 ug/L, which exceeded the hardness adjusted acute water quality criterion of 262 ug/L and the chronic criterion of 239 ug/L.

Arsenic concentrations increased from Linton Creek to the Metaline Mine. During low flow, arsenic concentrations in the Metaline Mine increased about 6-fold and during high flow by 16-fold over the concentrations in Linton Creek. Cadmium was not detected in Linton Creek. Thus, the concentration of cadmium in the Metaline Mine discharge increased by over 38-fold at low flow and by over 54-fold during high flow, but did not exceed the hardness adjusted water quality criteria. The concentration of lead increased during low flow by more than 90-fold from Linton Creek to the Metaline Mine. During high flow, the concentration increased by less than 2-fold. The concentration of lead in the mine discharge was higher during low flow than during high flow, while in Linton Creek the reverse was observed with a more than 14-fold increase during high flow.

Table 21. Metals Concentrations in Pend Oreille District/Metaline Mine Area Water Samples Collected October 2002 and May 2003 (µg/L)

Metaline Mine **2.80 4.48 0.755 1.08 1.81 0.475** 0.002U 0.002U

Metals detections highlighted in **BOLD**

 $* =$ exceeds water quality standard or guideline

Substantial contrasts in sediment quality were found between the background sample in Linton Creek and the Metaline Mine (Table 22). Cadmium increased from 0.68 mg/Kg in Linton Creek to 9.67 mg/Kg in the mine drainage, which exceeded the recommended sediment quality standard (SQS) of 0.6 mg/Kg and the cleanup screening level (CSL) of 1.0 mg/Kg. Zinc increased 10-fold from 377 mg/Kg to 3770 mg/Kg, with both values exceeding the SQS of 140 mg/Kg and the CSL of 160 mg/Kg. Lead increased from 171 mg/Kg in the upgradient sample to 751 mg/Kg in the Metaline Mine sample. The mine sample exceeded the SQS of 335 mg/Kg and the CSL of 430 mg/Kg. Mercury increased nearly 3-fold to 0.113 mg/Kg from Linton Creek to the Metaline Mine, but did not exceed the SQS of 0.5 mg/Kg or the CSL of 0.75 mg/Kg.

Table 22. Metals Concentrations in Pend Oreille District/Metaline Mine Area Sediment Samples Collected October 2002 (mg/Kg, dry)

Metals detections highlighted in **BOLD**

 $* =$ exceeds sediment quality guideline

 $J =$ estimated value

6. Chewelah District, Stevens County

Geology and Historical Mining Operations and Practices

The United Copper Mine was acquired by Judge Shapler of Chewelah in 1891 (Wolff et al., 2003). There are 24 mines and prospects in the United Copper Group. The principal mines are the United Copper, Amazon, Copper King, Keystone, and Chinto (Wolff et al., 2003).

Six prominent mineralized quartz veins with minor calcite and siderite have been identified and developed within the United Copper Group. The veins follow nearly vertical shear zones and partial replacement along bedding and jointing planes in schist and argillite of the Precambrian Belt series (Wallace Fm.) (Clark and Miller, 1975). Mineralization is probably related to the upper Mesozoic Flowery Trail granodiorite batholith that crops out two miles southeast of the mine workings along the Thompson Creek valley (Clark and Miller, 1968). The mines are developed along a series of sub-parallel, near vertical veins that strike north to northeast. The United Copper vein is 5 to 20 ft wide, averaging 8 ft wide. Ore is localized in a second-stage mineralization of silver rich tetrahedrite 2 to 12 inches wide (Huntting, 1956).

United Copper Co. produced over 9 million lbs of copper and 1.6 million ounces of silver from 1906 to 1920. Combined production from the Copper King, Amazon, Keystone, and Copper Queen was 18,000 tons or 5% of the output from the United Copper Group (Fulkerson and Kingston, 1958).

Commodities were copper, silver, and gold. Ore minerals include chalcopyrite, tetrahedrite and malachite. Non-ore minerals are pyrite, arsenopyrite, quartz, calcite, and siderite (Derkey et al., 1990).

Evaluation of Water Samples

Water quality samples were collected from the Copper King No. 2 Mine drainage, the Keystone Mine drainage, and from Nance Springs (Figure 6). The mines discharge to the drainage that contains Nance Springs, but the stream is intermittent in the vicinity of the mines. Water quality from the mine samples was compared to each other and to results from Nance Springs to determine whether mine drainage affected the water quality of the springs. Sediment samples were collected in the intermittent drainage above the Keystone Mine and below Nance Springs for comparison of upstream and downstream sediment quality. The Keystone Mine is located upstream of the Copper King No. 2 Mine.

For field parameters, Nance Springs resembles the Keystone Mine more than the Copper King. During low flow, Nance Springs and the Keystone Mine had similarly higher pH values than recorded in the Copper King, and during high flow had similarly lower values than the Copper King. Conductivity had the same pairing of Nance Springs with the Keystone, contrasting their relatively low measurements with high conductivity measurements in the Copper King during both low flow and high flow. TDS followed the same pattern as the conductivity, but sulfate diverged somewhat.

Figure 6. Location of Water and Sediment Samples Collected in Nance Springs and Two Mines, Chewelah District.

Seasonally, the concentration of sulfate in Nance Springs and the Keystone Mine showed little change. However, the concentration in Nance Springs was about 3-fold greater than the concentration in the Keystone Mine during both low flow and high flow. The concentration of sulfate did change seasonally in the Copper King mine. As a result, during low flow the concentration of sulfate in the Copper King was about 8-fold greater than the Keystone Mine and more than 2-fold above the concentration in Nance Springs. During high flow, the Copper King sulfate concentration was 14-fold greater than the Keystone Mine and 5-fold greater than Nance Springs.

Detections highlighted in **BOLD**

 $J =$ estimated value

 $U =$ not detected at or above the reported value

 UJ = not detected at or above the reported estimated value

The concentration of aluminum in Nance Springs of 110 ug/L at high flow represents more than a 5-fold increase over the Copper King Mine discharge. The concentration was more than a 2-fold increase above the Keystone Mine discharge and was above the Canadian guideline of 100 ug/L but below the EPA guideline of 750 mg/L. In contrast, during low flow, aluminum was not detected in the samples. Iron increased seasonally from low flow to high flow in all three sites. The concentration of iron in the Copper King discharge increased about 6-fold from low flow to high flow while Nance Springs increased about 8-fold. The iron concentration slightly exceeded the Canadian guideline of 300 ug/L but did not exceed the EPA guideline of 1000 ug/L. The concentration of iron in the Keystone Mine discharge increased about 3-fold during the same time and did not exceed guidelines.

Among the three sample sites, copper concentration was lowest in the Keystone Mine during both sample events. The concentration of copper in Nance Springs increased 25-fold above the Keystone Mine concentration during high flow and 8-fold during low flow. In turn, the concentration of copper in the Copper King increased 8-fold over Nance Springs at high flow and 20-fold during low flow. Further illustrating the difference between the mines, the concentration of copper during low flow in the Copper King discharge increased 157-fold over the concentration in the Keystone Mine and 220-fold during high flow.

Zinc concentrations were higher in the mines than in Nance Springs during both low flow and high flow. During high flow, the Copper King Mine and Keystone Mine zinc concentrations were more than 14-fold higher than in Nance Springs. Zinc increased 3-fold from low flow to high flow in the Copper King. There was little change seasonally in Nance Springs or the Keystone Mine. Arsenic was not detected in the Keystone Mine, but was present in the Copper King and Nance Springs during both low flow and high flow. The arsenic concentration in the Copper King was higher by from 5-fold to 8-fold above the concentration in Nance Springs.

Replicate water samples were collected from the Copper King No. 2 Mine discharge during low-flow conditions to assess variability of metals and general chemistry concentrations (Table 25). The measured variability was low. Similarly, discharge from the Keystone Mine was sampled during high-flow conditions. Lead showed the greatest variability. The concentrations in Tables 23 and 24 represent averaged concentrations.

Table 24. Metals Concentrations in Chewelah District Water Samples Collected October 2002 and May 2003 (µg/L)

Metals detections highlighted in **BOLD**

Location		Copper King No. 2 Mine		Keystone Mine			
Date		$03-Oct-02$			20-May-03		
Sample No.	408428	408430	RPD	214082	214083	RPD	
TSS (mg/L)	1U	1U	- -	3	3	0%	
TDS (mg/L)	515	512	1%	183	183	0%	
Sulfate (mg/L)	85.1	88.1	3%	11.1	11.2	1%	
Turbidity (mg/L)	0.5UJ	0.5UJ	- -	1.2J	1.2J	0%	
Iron $(\mu g/L)$	56	53	6%	190	170	11%	
Aluminum $\left(\frac{u g}{L}\right)$	25U	25U	- -	57	51	11%	
Zinc (ug/L)	6.9	6.3	9%	17.6	16.8	5%	
Copper $\left(\frac{ug}{L}\right)$	29.9	29.8	0%	0.14	0.12	15%	
Arsenic (ug/L)	6.11	6.21	2%	0.01U	0.01U	- -	
Cadmium $\left(\frac{u g}{L}\right)$	0.059	0.057	3%	0.020U	0.020U		
Lead (ug/L)	0.02U	0.02U	- -	0.035	0.020U	$>55\%$	
Mercury (ug/L)	0.006	0.006	2%	0.0020U	0.0020U	- -	
Hardness (mg/L)	439	434	1%	153	152	1%	

Table 25. Results from Field Replicates on Water Samples in Chewelah District Collected October 2002 and May 2003

Metals detections highlighted in **BOLD**

RPD = relative percent difference (range as percent of duplicate mean)

 UJ = not detected at or above the reported estimated value

In Nance Springs, antimony, copper, and silver were found in concentrations exceeding the recommended sediment quality standards (SQS). Antimony was not detected in the upstream sample above the Keystone Mine at 0.2 mg/Kg while the Nance Springs antimony concentration was 3.03 mg/Kg. This value exceeded the SQS of 0.4 mg/Kg and the cleanup screening level (CSL) of 0.6 mg/Kg. Copper increased 10-fold downstream to 290 mg/Kg, which exceeded the SQS of 80 mg/Kg but not the CSL of 830 mg/Kg. Silver was not detected in the upstream sample at 0.1 mg/Kg, but increased to 2.46 mg/Kg in Nance Springs, slightly exceeding the SQS of 2 mg/Kg and nearly equal to the CSL of 2.5 mg/Kg. Arsenic increased more than 2-fold downstream to 8.95 mg/Kg but did not exceed the SQS of 20 mg/Kg or the CSL of 51 mg/Kg. Sediment samples were not collected at the Keystone Mine or the Copper King Mine.

Table 26. Metal Concentrations in Chewelah District Sediment Samples Collected October 2002 (mg/Kg, dry)

Sample Location	Al	Sb	Be	C _d	Cr	Cu	Fe
Above Keystone Mine	5130	.02U	0.26	0.1U	6.19	28.8	15800
Nance Springs	4840	$3.03*$	0.26	0.11	6.17	$290*$	19800
Sample Location	Mn	Ni	Ag	Zn	As	Pb	Hg
Above Keystone Mine	304	6.49	0.1U	11.2	3.57	4.43	0.016
Nance Springs	582	6.32	$2.46*$	21.4	8.95	2.75	0.014
Sample Location	Se	TI					
Above Keystone Mine	0.5U	0.12					
Nance Springs	0.5U	0.1U					

Metals detections highlighted in **BOLD**

 $* =$ exceeds sediment quality guideline

 $J =$ estimated value

7. Republic District, Ferry County

Geology and Historical Mining Operations and Practices

Gold was discovered while the area that includes the Republic District was part of the Colville Indian Reservation. When the northern half of the reservation was opened to prospecting on February 21, 1896 all the principal veins were claimed in a few weeks (Full and Grantham, 1968). There are a multitude of mines and prospects in the area. The principal mines in the early years were the Knob Hill, Lone Pine, Quilp, and Republic. Three mills were built during the early years, and considerable ore was handled (Staatz and Pearson, 1990).

The Republic District is located in the Republic Graben, a north trending, fault-bounded structural low. The Okanogan dome is to the west and the Kettle dome is east of the district. The dominant rocks in the Republic District are greenschist facies rocks, clastic and volcaniclastic and volcanics, amphibolite facies metamorphic rocks, and granitic plutons of the Okanogan and Kettle metamorphic core complexes (Cheney and Rasmussen, 1996). There is no current mining activity in the vicinity of the project sample sites.

Gold and silver is the principal mineralization in the district which occurs in Eocene epithermal veins (Lasmanis, 1996). Epithermal vein deposits (metal-bearing hot springs) have been the mainstay of production from the district. The Knob Hill Mine, which was the longest producing mine in the western part of the district, was in production from 1910 until 1995. A cyanide mill was added to the operation in 1937 (Lasmanis, 1996). Flotation cells were added in 1940. The principal ore minerals are gold, electrum, tellurides, chalcopyrite, stibnite, realgar, tetrahedrite, polybasite, pyrargyrite, argentite, umangite, and naumannite. Host rocks for the deposits are dacite and andesite flows, breccias, tuffs, and tuff breccias of the Eocene Sanpoil Formation (Derkey et al., 1990).

Replacement/exhalative deposits also occur in the eastern part of the Republic District (Derkey, 1994). These deposits occur at the contact between carbonate and clastic sedimentary rocks. Gold is sporadically distributed in massive iron oxide-sulfide zones in carbonate rocks, and in stockworks of pyrrhotite and quartz-sulfide veinlets (mostly pyrite) in clastic sedimentary rock (Derkey, 1994). Deposits of this type have been mined at the Overlook, Lamefoot, and Key mines. These deposits are enriched in gold, silver, copper, and iron. Ore minerals consist of pyrite, pyrrhotite, magnetite, and chalcopyrite. Host rocks for the deposits are unnamed Permian-Triassic greywacke, argillite, cherts, and limestone (Derkey et al., 1990).

Evaluation of Water Samples

Water and sediment quality samples were collected in Granite Creek near the town of Republic. An upstream reach of Granite Creek was also sampled as part of a previous study (Raforth et al., 2000). The previous study included one sample about two miles upstream of the upstream sample in this study (Figure 7). Samples obtained in this study were from a different part of the district where tailings from historic mining operations were deposited on the right bank of Granite Creek.

Figure 7. Location of Water and Sediment Samples Collected in Granite Creek, Republic District.

For field parameters, pH was very slightly lower in the downstream sample than in the upstream sample during both low flow and high flow (Table 27). Low-flow pH readings were somewhat higher than the high-flow readings at both the upstream and downstream sites. Conductivity was also slightly lower in the downstream sample during low flow and high flow, and was substantially lower during high flow. Comparing the field parameters from this study to the previous study, the pH values in this study were slightly higher and the conductivity measurements were about the same. TDS and sulfate concentrations were about the same upstream and downstream during low flow and high flow, but the concentrations were lower during high flow than low flow. The concentration of sulfate increased 2-fold downstream from the sample site in the previous study.

Detections highlighted in **BOLD**

 $J =$ estimated value

 $U = not detected at or above the reported value$

 UJ = not detected at or above the reported estimated value

Aluminum concentrations exceeded the guidance value of 750 ug/L in both the upstream and downstream samples during high flow (Table 28). Aluminum was not detected in the low-flow samples at a detection limit of 25 mg/L. Iron and copper varied little between the upstream and downstream sample sites during both low flow and high flow. However, iron concentration increased by more than 15-fold from low flow to high flow. The concentration of iron was about 50% higher in the current study than in the previous study. The upstream and downstream samples in this study, and the downstream sample in the previous study, exceeded the Canadian guideline for iron of 300 ug/L but not the EPA guideline of 1000 ug/L. The copper concentration also showed an increase of more than 2-fold from low flow to high flow. Copper concentration was slightly lower in this study than the previous study.

For zinc, concentrations decreased slightly downstream and were slightly higher in high flow than in low flow. Zinc was higher in the previous study. Arsenic concentrations were about the same between the upstream and downstream samples, but were higher in the low-flow samples than the high-flow samples. The low-flow arsenic concentration in this study showed an increase of about 3-fold over the previous study. Cadmium and lead were detected in the high-flow sample but not detected in the low-flow samples. The high-flow cadmium and lead concentrations in this study were lower than the concentrations in the previous study. Mercury did not vary significantly between the upstream and downstream samples during either low flow or high flow. The high-flow concentration was increased about 5-fold over the low-flow concentration and was higher than the concentration in the previous study.

Table 28. Metals Concentrations in Republic District Water Samples Collected October 2002 and May 2003 (µg/L)

Metals detections highlighted in **BOLD**

 $* =$ exceeds water quality standard or guideline

The recommended sediment quality standards (SQS) for antimony, silver, and arsenic were exceeded in Granite Creek (Table 29). The concentration of antimony decreased downstream, but both upstream and downstream results exceeded the SQS of 0.4 mg/Kg and the cleanup screening level (CSL) of 0.6 mg/Kg. For silver, the concentration increased nearly 5-fold to 3.21 mg/Kg, which exceeded the SQS of 2 mg/Kg and the CSL of 2.5 mg/Kg. Arsenic increased from 17.4 mg/Kg in the upstream sample to 41.9 mg/Kg in the downstream sample, exceeding the SQS of 20 mg/Kg but not the CSL of 51 mg/Kg. The concentration of copper, lead, and selenium increased about 2-fold downstream but did not exceed the SQS or CSL. Mercury increased nearly 17-fold downstream to 0.354 mg/Kg. This result was slightly below the SQS of 0.5 mg/Kg and was the highest value obtained in this study.

The previous study also obtained a sediment sample in Granite Creek, upstream of this study. With the exception of cadmium, which was not detected in either study, the results at the sample sites for all parameters in the current study were elevated compared to the previous study. The concentration of copper in the previous study was 2.9 mg/Kg, while in this study the comparable upstream sample result was 5.73 mg/Kg. The concentration of arsenic in the previous study was 2.3 mg/Kg, and in this study was 17.4 mg/Kg in the upstream sample. Mercury was not detected at 0.005 mg/Kg in the previous study, but increased downstream to 0.021 mg/Kg in the upstream sample in the current study. The results from these two datasets suggest that there is a sediment source contributing metals to Granite Creek that is located between the two sample sites.

Table 29. Metal Concentrations in Republic District Sediment Samples Collected October 2000 (mg/Kg, dry)

Metals detections highlighted in **BOLD**

 $* =$ exceeds sediment quality guideline

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8. Money Creek District, King County

Geology and Historical Mining Operations and Practices

Originally discovered in 1889 and closed in 1941, the Apex Gold Mines Inc. was the last major producer in the district and was dissolved in 1943. The mine has a scattered history of production owing to periods of changing ownership and its isolated location in mountainous country (Wolff et al., 2001).

The Apex Mine occurs in Miocene granitic rocks of the Snoqualmie batholith. The Snoqualmie batholith is part of early magmatism of the Cascade magmatic arc (Tabor et al., 1993). Mineralization is concentrated in discontinuous ore shoots along strike of a fissure traceable for 1000 ft on the surface. Mineralization is in a quartz vein 2-6 ft wide (Huntting, 1956).

Five adits totaling 2,950 ft of haulage tunnel and 5,000 ft of development were dug at the Apex Mine. Adit 3 discharges water and adit 4, which has standing water, lies in a vertical wall 10 ft above Milwaukee Creek (Wolff et al., 2001). The mine produced about \$300,000 at historic metal prices (Livingston, 1971).

Ore minerals are chalcopyrite, galena, sphalerite, tetrahedrite, and stibnite. Non-ore minerals are pyrite, arsenopyrite, arsenolite, quartz, tourmaline, and calcite (Derkey et al., 1990).

Evaluation of Water Samples

Water quality and sediment quality samples were obtained at the head of Milwaukee Creek and downstream of the Apex Mine (Figure 8). There was one abandoned mine working uphill from the upstream sample site, but it was not discharging to Milwaukee Creek. Sampling was conducted during high flow and low flow for water quality, and during low flow for sediment quality.

For field parameters, pH and conductivity did not vary significantly between the upstream and downstream samples during either low flow or high flow (Table 30). The TDS concentration was higher downstream during high flow, but was about the same concentration in the upstream and downstream samples during low flow. TDS concentration increased by 2- or 3-fold during high flow above the low-flow concentrations at the upstream and downstream sample sites. Sulfate increased more than 5-fold downstream during both low flow and high flow.

Figure 8. Location of Water and Sediment Samples Collected in Milwaukee Creek, Money Creek District.

Table 30. Field Measurements and General Chemistry Results for Money Creek District Water Samples Collected October 2002 and June 2003

Detections highlighted in **BOLD**

 $J =$ estimated value

 $U =$ not detected at or above the reported value

 UJ = not detected at or above the reported estimated value

The concentration of copper increased 19-fold downstream during low flow. The concentration of 2.08 ug/L exceeded the hardness adjusted acute and chronic water quality criteria (Table 31). During high flow, at the upstream site, copper concentration exceeded the hardness adjusted acute and chronic water quality criteria and the downstream sample exceeded the chronic criterion only.

During low flow, the concentration of zinc increased about 30-fold downstream. The downstream sample result of 56.7 ug/L substantially exceeded the hardness adjusted acute and chronic water quality criteria of 13.2 ug/L and 12.1 ug/L respectively. During high flow, the upstream sample result of 16.3 ug/L exceeded the acute water quality criterion of 5.77ug/L and the chronic criterion of 5.26 ug/L. The high-flow downstream sample result of 45.2 ug/L substantially exceeded the acute criterion of 9.67 ug/L and the chronic criterion of 8.83 ug/L.

Arsenic increased downstream by more than 2-fold during high flow and nearly 2-fold during low flow. Cadmium in the upstream and downstream samples exceeded the hardness adjusted water quality acute and chronic criteria at high flow and at low flow. Lead exceeded the hardness adjusted water quality chronic criterion during high flow in the upstream sample. During low flow, lead increased downstream more than 2-fold, but did not exceed water quality criteria.

Replicate water samples were collected at the downstream sample site in Milwaukee Creek to estimate general chemistry and metals variability (Table 32). There was negligible variability in the samples. The data in Tables 30 and 31 show the average of these values.

Table 31. Metals Concentrations in Money Creek District Water Samples Collected October 2002 and June 2003 (µg/L)

Metals detections highlighted in **BOLD**

 $* =$ exceeds water quality standard or guideline

 $U =$ not detected at or above the reported value

Table 32. Results from Field Replicates on Water Samples in Money Creek District Collected June 2003

Metals detections highlighted in **BOLD**

RPD = relative percent difference (range as percent of duplicate mean)

Antimony, cadmium, zinc, and arsenic exceeded the recommended sediment quality standards (SQS) and the cleanup screening levels (CSL) (Table 33). Antimony increased from 0.99 mg/Kg in the upstream sample to 2.41 mg/Kg in the downstream sample. Both of these values exceeded the SQS of 0.4 mg/Kg and the CSL of 0.6 mg/Kg. Cadmium increased downstream nearly 7-fold to 1.49 mg/Kg which exceeded the SQS of 0.6 mg/Kg and the CSL of 1.0 mg/Kg. The concentration of copper in the downstream sample slightly exceeded the SQS of 80 mg/Kg but not the CSL of 830 mg/Kg. The concentration of zinc increased more than 4-fold to 346 mg/Kg which exceeded the SQS of 140 mg/Kg and the CSL of 160 mg/Kg.

	Al	Sb	Be	Cd	Cr	Cu	Fe
Sample Location							
Milwaukee Crk Up	8830	$0.99*$	0.1U	0.22	8.1	54.3	17900
Milwaukee Crk Down	9470	$2.41*$	0.1U	$1.49*$	16.0	$83.1*$	19000
Sample Location	Mn	Ni	Ag	Zn	As	Pb	Hg
Milwaukee Crk Up	284	4.28	0.14	74.8	$169*$	20.5	0.0682
Milwaukee Crk Down	376	4.86	0.13	$346*$	$230*$	73.0	0.016
Sample Location	Se	TI					
Milwaukee Crk Up	0.62	0.16					
Milwaukee Crk Down	0.5U	0.13					

Table 33. Metals Concentrations in Money Creek District Sediment Samples Collected October 2002 (mg/Kg, dry)

Metals detections highlighted in **BOLD**

 $* =$ exceeds sediment quality guideline

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9. Index District, Snohomish County

Geology and Historical Mining Operations and Practices

Arthur Egbert discovered the Sunset outcrop in June 1897 (Patty, 1921). That same year, Sunset Copper Co. was formed and remained the principal owner-operator from 1902 through 1935. Kromona mines operated a lease during World II. The last documented production was in 1946 (Wolff et al., 2002). The Sunset Mine led the state in production of copper from 1902 to 1946. Data from smelter returns indicate a total recovery during this period of 12,912,000 lbs of copper, 156,000 oz of silver, and 1500 oz of gold (Huntting, 1956).

The ore occurs as lenticular masses in six roughly parallel shear zones containing chalcopyrite and bornite (Wolff et al., 2002). The host rock is granodiorite, identified as the Oligocene Index batholith (Tabor et al., 1990). The veins strike $N60^{\circ}$ W and dip 80 $^{\circ}$ NE. Most production came from the Sunset vein. It varied from 6 to 30 ft in width, with a pay streak 6 to 8 ft wide (Campbell, 1938).

Ore minerals are chalcopyrite, bornite, molybdenite, silver, and copper. Non-ore minerals are pyrite, quartz, calcite, marcasite, serpentine, talc, chlorite, and kaolinite in a gangue of altered granodiorite (Derkey et al., 1990). The absence of arsenopyrite at the mine presents an interesting departure from ores in the nearby Monte Cristo and Money Creek districts (Wolff et al., 2002).

Evaluation of Water Samples

For the Index District, water and sediment quality samples were collected in Trout Creek, upstream and downstream of the discharge from the Sunset Mine. Samples were also collected in the mine drainage for comparison to the downstream water quality results (Figure 9). Sediment samples were taken during low flow in Trout Creek.

For field parameters, there was little variation in pH among the upstream, downstream, and Sunset Mine measurements (Table 34). The pH in the mine drainage decreased slightly during low flow from the high flow measurement. Conductivity in the mine drainage did contrast significantly with the receiving water. The conductivity of the mine drainage increased from the upstream measurement by more than 8-fold during high flow and nearly 7-fold during low flow. Conductivity measurements in Trout Creek showed little variation between high flow and low flow. TDS in Trout Creek showed little variation between upstream and downstream samples or between high-flow and low-flow conditions. TDS in the mine drainage increased 4-fold during high flow and 6-fold during low flow over the upstream samples. Sulfate increased downstream during high flow and low flow. The concentration of sulfate in the mine drainage increased nearly 12-fold during high flow and nearly 9-fold during low flow when compared to the upstream samples.

Figure 9. Location of Water and Sediment Samples Collected in Trout Creek, Index District.

Table 34. Field Measurements and General Chemistry Results for Index District Water Samples Collected October 2002 and June 2003

Detections highlighted in **BOLD**

 $J =$ estimated value

 $U =$ not detected at or above the reported value

 UJ = not detected at or above the reported estimated value

 $NM = not measured$

Copper concentration increased nearly 12-fold between the upstream and downstream samples during both high-flow and low-flow conditions (Table 35). Comparing the upstream samples and the mine drainage samples, copper increased more than 246-fold during high flow and more than 283-fold during low flow. The downstream and mine drainage samples exceeded the hardness adjusted water quality criteria. During high flow, the copper concentration of 4.51 ug/L in the downstream sample exceeded the hardness adjusted chronic criterion of 1.52 ug/L and the acute criterion of 1.85 ug/L. Also during high flow, the mine drainage concentration of 93.7 ug/L exceeded the chronic criterion of 11.4 ug/L and the acute criterion of 7.9 ug/L. During low flow, the concentration of copper of 4.99 ug/L in the downstream sample exceeded the chronic criterion of 1.88 ug/L and the acute criterion of 2.34 ug/L. The low-flow mine drainage concentration of 119 ug/L exceeded the chronic criterion of 8.6 ug/L and the acute criterion of 12.6 ug/L. Copper concentrations were slightly higher during low flow than during high flow.

Arsenic increased from the upstream sample to the mine drainage by 18-fold during high flow and by 16-fold during low flow. Concentrations were slightly lower during high flow than during low flow. Arsenic increased slightly from upstream to downstream during both low flow and high flow. Comparing the upstream samples to the mine drainage samples showed that cadmium increased more than 4-fold during high flow and more than 6-fold during low flow, but did not change between the upstream and downstream samples. Mercury increased more than 2-fold during high flow and more than 3-fold during low flow from upstream to the mine drainage. There was no detectable change in concentration between the upstream and downstream samples.

Table 35. Metals Concentrations in Index District Water Samples Collected October 2002 and June 2003 (µg/L)

Metals detections highlighted in **BOLD**

 $* =$ exceeds water quality standard or guideline

 $U =$ not detected at or above the reported value

Replicate samples were obtained to estimate the variability in general chemistry and metals concentrations at the downstream Trout Creek sample site during high-flow conditions and from the Sunset Mine discharge during low-flow conditions (Table 36). In the downstream high-flow samples, zinc and arsenic exhibited the greatest variability. Mercury in the Sunset Mine discharge showed the most variability. The concentrations in Tables 34 and 35 represent average concentrations.

Location	Sunset Mine			Trout Creek Down			
Date		$09-Oct-02$		23 -Jun-03			
Sample No.	418239	418241	RPD	264085	264086	RPD	
TSS (mg/L)	1U	1U		1	1U		
TDS (mg/L)	91	90	1%	20	16	22%	
Sulfate (mg/L)	11.7	11.7	0%	1.4	1.4	0%	
Turbidity (mg/L)	0.5UJ	0.5UJ	$ -$	0.5J	0.5U		
Iron $(\mu g/L)$	25U	25U		50U	50U		
Aluminum $\left(\frac{u g}{L}\right)$	25U	25U	- -	50U	50U		
Zinc (ug/L)	3.5	3.3	6%	3.2	1.4	78%	
Copper (ug/L)	118	119	1%	4.56	4.46	2%	
Arsenic (ug/L)	4.15	$\overline{\mathbf{4}}$	2%	0.25	0.40	46%	
Cadmium (ug/L)	0.13	0.13	0%	0.020U	0.020U	$ -$	
Lead (ug/L)	0.027	0.031	14%	0.023	0.020U		
Mercury (ug/L)	0.0037	0.0059	46%	0.0020U	0.0020U		
Hardness (mg/L)	72.8	72.4	1%	9.39	9.58	2%	

Table 36. Results from Field Replicates on Water Samples in Index District Collected October 2002 and June 2003

Metals detections highlighted in **BOLD**

RPD = relative percent difference (range as percent of duplicate mean)

 $U = not detected at or above reported value$

 UJ = not detected at or above the reported estimated value

Evaluation of Sediment Samples

Copper and zinc were the only metals that exceeded the recommended sediment quality standards (SQS) in Trout Creek (Table 37). Copper increased from 131 mg/Kg in the upstream sample to 210 mg/Kg in the downstream sample. Both values exceeded the SQS of 80 mg/Kg but not the CSL of 830 mg/Kg. The concentration of zinc increased more than 4-fold to 439 mg/Kg in the downstream sample which exceeded the SQS of 140 mg/Kg and the CSL of 160 mg/Kg. Arsenic increased nearly 2-fold downstream to 19 mg/Kg, nearly equivalent to the SQS of 20 mg/Kg and less than the CSL of 51 mg/Kg. No sediment sample was collected from the Sunset Mine.

A replicate sediment sample was collected at the downstream Trout Creek sample site during low-flow conditions. Zinc, mercury, and arsenic showed the greatest variability.

Sample Location	Al	Sb	Be	C _d	Cr.	Cu	Fe
Trout Crk Up	9900	0.22	0.10	0.21	17.6	$131*$	19200
Trout Crk Down	11800	0.2U	0.14	0.25	22.8	$210*$	22300
Sample Location	Mn	Ni	Ag	Zn	As	Pb	Hg
Trout Crk Up	561	16.1	0.57	97.9	10.2	7.17	0.028
Trout Crk Down	483	21.9	0.23	439*	19.0	12.1	0.048
Sample Location	Se	T1					
Trout Crk Up	0.5U	0.1U					
Trout Crk Down	0.5U	0.1					

Table 37. Metals Concentrations in Index District Sediment Samples Collected October 2002 (mg/Kg, dry)

Metals detections highlighted in **BOLD**

 $* =$ exceeds sediment quality guideline

 $U = Not detected at or above the reported value$

Metals detections highlighted in **BOLD**

RPD = relative percent difference (range as percent of duplicate mean)

 $U = not detected at or above reported value$

10. Mount Baker District, Whatcom County

Geology and Historical Mining Operations and Practices

W.H. Norton discovered the Great Excelsior Mine in 1900. The mine was also known as the Lincoln, President, Excelsior, and Wells Creek. In 1902 the Great Excelsior Mining Co. was incorporated, and a 20-stamp mill was built. In 1914 a new cyanide mill was installed which replaced the amalgamation mill used earlier. Because of poor recoveries, the mill was modified for flotation but this also proved impractical (Moen, 1969).

This epithermal deposit consists of sulfide cemented brecciated veins also on a shear zone. The main fracture system extends 4,000 ft and has a width of 200-400 ft. The fractures are lined with quartz, pyrite, and other sulfides. The brecciated zone, as exposed in the Big Stope Mine workings, is 400 ft long by 270 ft wide and has been explored to a depth of 325 ft. The breccia consists of .25-1 in. fragments of volcanic rocks, quartz, and slate. The higher-grade ore occurs in felsic and tuffaceous breccia. In 1934 approximately 200 channel and crosscut samples of underground workings gave an average of 0.09 oz/ton of gold and 0.75 oz/ton of silver, and outlined a reserve of 1,250,000 tons of ore from the lowest mine workings to the surface (Moen, 1969).

Rocks of the Jurassic Wells Creek Volcanics have been tightly folded in a west-plunging syncline that is superimposed on the west limb of a larger regional north trending anticline. The volcanic rocks were deposited in a marine volcanic setting (Tabor, 1994)

Ore minerals occur in andesite, felsites, tuffs, and slate and consist of chalcopyrite, galena, sphalerite, tellurides, silver, and tetrahedrite. Non-ore minerals are pyrite, arsenopyrite, quartz, and dolomite (Derkey et al., 1990).

Evaluation of Water Samples

Water and sediment quality samples were collected in Wells Creek, upstream and downstream from the apparent point of discharge from the Excelsior Mine and mill (Figure 10). No tailings were observed at the site, although pieces of a large diameter pipe were found on the hillside where the former mill was located. Sediment quality samples were collected during low flow.

For field parameters, there was little change in pH or conductivity between either the upstream and downstream samples or between the high-flow and the low-flow samples (Table 39). Conductivity measurements were similar, with slightly lower conductivity during high-flow conditions.

Figure 10. Location of Water and Sediment Samples Collected in Wells Creek, Mount Baker District.

Table 39. Field Measurements and General Chemistry Results for Mount Baker District Water Samples Collected October 2002 and June 2003

Detections highlighted in **BOLD**

 $J =$ estimated value

There was little of note in the water quality samples analyzed for metals (Table 40). Aluminum concentrations upstream and downstream, during both low flow and high flow, exceeded the Canadian guideline of 100 ug/L, but not the EPA guideline of 750 ug/L. Iron concentrations increased overall during low flow when compared to high flow, but showed little change between upstream and downstream samples. At low flow, the iron concentration in the upstream and downstream samples exceeded the Canadian guideline of 300 ug/L, but not the EPA guideline of 1000 ug/L. Copper, zinc, and arsenic were detected, but showed little change between upstream and downstream samples or between high-flow and low-flow conditions.

Table 40. Metals Concentrations in Mount Baker District Water Samples Collected October 2002 and June 2003 (µg/L)

	Aluminum (total recoverable)		Iron (total recoverable)		Copper (dissolved)		Zinc (dissolved)	
Sample Location	Low Flow	High Flow	Low Flow	High Flow	Low Flow	High Flow	Low Flow	High Flow
Wells Creek Up	591	480	505	160	0.17	0.19	1U	1.5
Wells Creek Down	649	390	530	140	0.18	0.18	1.4	1.6
	Arsenic		Cadmium		Lead		Mercury	
	(dissolved)		(dissolved)		(dissolved)		(total recoverable)	
	Low	High	Low	High	Low	High	Low	High
Sample Location	Flow	Flow	Flow	Flow	Flow	Flow	Flow	Flow
Wells Creek Up	0.25	0.22	0.02U	0.02U	0.02U	0.02U	0.002U	0.002U
Wells Creek Down	0.24	0.23	0.02U	0.02U	0.02U	0.02U	0.002U	0.002U

Metals detections highlighted in **BOLD**

 $U =$ not detected at or above the reported value

Evaluation of Sediment Samples

None of the recommended sediment quality standards or cleanup screening levels were exceeded in upstream or downstream samples on Wells Creek (Table 41). There was no significant contrast between the upstream and downstream samples, although all metals except antimony, silver, selenium, and thallium were detected in the samples.

A replicate sediment sample was collected during low-flow conditions at the downstream sample site (Table 42). Arsenic and mercury exhibited the greatest variability. Table 41 contains the averaged metals concentrations.

Table 41. Metal Concentrations in Mt Baker District Sediment Samples Collected October 2002 (mg/Kg, dry)

Metals detections highlighted in **BOLD**

 $U = Not detected at or above the reported value$

Location	Wells Creek Downstream					
Date	02 -Oct- 02					
Sample No.	418249	418250	RPD			
Antimony	0.2U	.02U				
Arsenic	13.3	9.83	30%			
Chromium	14.4	16.6	14%			
Cadmium	0.15	0.15	0%			
Silver	0.1U	0.1U				
Selenium	0.5U	0.5U				
Zinc	63.7	65.3	2%			
Copper	22.7	22.7	0%			
Beryllium	0.20	0.22				
Lead	4.11	4.37	6%			
Thallium	0.1U	0.1U	- -			
Aluminum	16800	17600	5%			
Iron	28600	30700	7%			
Manganese	469	485	3%			
Mercury	0.016	0.021	27%			
Nickel	11.7	12.2	4%			

Table 42. Results from Field Replicates on Sediment Samples Mount Baker District Collected October 2002 (mg/Kg, dry)

Metals detections highlighted in **BOLD**

RPD = relative percent difference (range as percent of duplicate mean)

 $U = not detected at or above reported value$

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Discussion

Low Level Metals Sampling

The results of the sampling for this project illustrated the value of low-level metals sampling in metals mining districts. Water quality studies of metals mines that do not employ this sampling and analysis method would be hampered by detection limits that exceed one or more regulatory criteria. In many cases, this scenario occurs for metals that require adjustment for hardness. In most mining districts, due to their geologic and physical setting, measured hardness concentrations are low. As a result, the hardness corrected metals criteria are correspondingly lowered, and standard detection limits are of limited or no application for comparing metals concentrations in receiving water to water quality criteria. This study was conducted at locations that were either not sampled previously, or the previous sampling program did not employ low level sampling and analysis methods and thus were not able to accurately characterize existing water quality conditions.

Seasonality of Water Quality Impacts

One objective of this study was the continued investigation of the applicability of a geochemical model that predicts seasonality of water quality impacts in metals mining districts. The model is based on the concept that during late fall and winter efflorescent sulfate salts form in mine fractures, tailings, and exposed rock surfaces due to the combination of evaporation and reduced infiltration and percolation of surface water. Efflorescent salts consist of precipitated metals and sulfate formed from the oxidation of ore-bearing minerals and pyrite. As water percolates into the pores and fractures during spring or early summer runoff, these salts are resolubilized and flushed from the mine workings, tailings, and waste rock piles. The result would be to increase metals concentrations discharged into an adjacent receiving water from the mine area. A critical driver for the model is adequate recharge into the mine workings to create a substantial flux of recharge that is able to resolubilize the salts, and transport the redissolved metals and sulfate into the adjacent receiving water. Similarly important is timing sample collection to coincide as nearly as possible with maximum flushing process. Geology and mineralogy of the ore deposit would likely have an effect on the model as well.

The authors' two previous studies gave apparently mixed results on this issue. Sampling conducted in 1997 (Raforth et al., 2000) supported the model and suggested a correlation between spring runoff conditions and increased water quality impacts. However, the conclusion drawn from the sampling results during the fall of 2000 and spring 2001 was that seasonality was not apparent in the data (Raforth et al., 2002). The explanation advanced was that, while the winter of 1996-1997 was one of heavy snow at high elevation and substantial spring precipitation and runoff at low elevation, the winter and spring of 2000-2001 consisted of record low precipitation and limited runoff.

Springtime sampling conducted during this project appears to have once again occurred following drought conditions, resulting in generally low spring runoff. The low recharge scenario could also result in a narrow window for sampling, or the dilution of the limited volume of discharge from the mine or other source. As a result, the seasonality of water quality impacts would be masked, and reliable conclusions on the efficacy of the model would be tenuous at best and wrong at the worst.

A few observations could be made from the data, however. The seasonal contrast for suspended solids was minimal to negligible during this study. This suggests a low volume of water moving through the mining districts during spring freshet, at the time when flushing of salts should have been maximized. The same observation can be made of the low contrast between spring and fall turbidity values, reinforcing the suspended solids results. The concentration of sulfate in the samples, whether measured during low-flow or high-flow conditions, was very low. Also, at most sites, the concentration of sulfate was higher during low flow than during high flow, contrary to the model but consistent with the low recharge scenario. Under the low recharge condition, streamflow would consist of runoff and baseflow. In that case, observed anomalies in surface water quality may represent the contribution of a steady-state load of contaminants from groundwater. This concept could only be verified by installing groundwater monitoring wells at selected sites.

Fingerprinting Acid Rock Drainage

Part of the geochemical model is also intended to pursue a method for fingerprinting water quality impacts from acid rock drainage (ARD). This part of the model is based on sulfate as a primary constituent of efflorescent mineralized salts formed during low-flow (non-recharging) conditions from oxidation of pyrite and ore minerals. When spring percolation resolubilizes the salts, sulfate is released and transported to the receiving water. Under the geochemical conditions observed at the sample sites, sulfate is expected to be conservative and remain in solution. It would then be detected in samples downstream from the mining operations. Other cations and anions are also released upon resolubilization of the salts, so that an increase in total dissolved solids (TDS) also occurs. However, since sulfate is the dominant constituent of the salts, the ratio of sulfate to TDS should increase. Accompanying the increase of sulfate would be an increase in the concentration of metals in the mine discharge water, and seasonally changing water quality impacts to the receiving water.

Using this aspect of the geochemical model, another goal of this study was to attempt to determine a threshold value for the sulfate:TDS ratio. Determining such a threshold value would be highly useful as a low-cost screening method for identifying mines or mining districts that require detailed sampling. The ratio method also depends on vigorous spring flushing of the efflorescent minerals into the receiving water. If adequate flushing does not occur, the ratio method would be inconclusive due to low sulfate concentration in the mine discharge. The first of the authors' screening studies, which appeared to exhibit seasonal water quality characteristics, suggested that a sulfate:TDS ratio greater than 20% would properly identify districts that were contributing to water quality impacts. From the second study, which did not have seasonal characteristics, an appropriate ratio could not be extracted from the data.

The results of this study in part appear to follow the inconclusive course of the second study for potentially the same reason. Analyzing the results of this study did not establish a clear threshold value for the ratio. Discharges from a few mines were sampled during this study as a direct measure of the fingerprinting method and as a comparison to results from the downstream receiving water sample because dilution also plays an unaccounted role in the model.

Here again the outcome showed mixed results. As an example, in the Chewelah District two adjacent mines were sampled along with a downstream spring. The comparison of results from the two adjacent mines illustrates the potentially local variability of sample results. At the Copper King No. 2 Mine, the low-flow concentration of 86.6 mg/L sulfate increased to 158 mg/L during high flow, while TDS decreased from 514 mg/L to 477 mg/L (Table 23). At the nearby Keystone Mine, the sulfate concentration was about 11 mg/L during both low-flow and high-flow conditions, substantially lower than the Copper King. TDS concentrations at the Keystone increased slightly from low flow to high flow, but were also substantially lower than the TDS concentrations found at the Copper King Mine during the same sampling events. Taken together, the low-flow sulfate:TDS ratio of 17% at the Copper King approached the threshold value of 20% previously recommended, and the high-flow ratio of 33% exceeded the threshold value (Appendix H). Meanwhile, the Keystone ratio was 6% for both high-flow and low-flow conditions, well under the threshold.

Referring to the metals concentrations associated with these sulfate:TDS ratios, zinc at the Copper King Mine increased 3-fold from low-flow to high-flow conditions, which is consistent with expectations from the model (Table 24). However, the highest zinc concentration did not exceed water quality standards. At the Keystone Mine, the zinc concentration did not change significantly between low flow and high flow, and was also about the same concentration as in the Copper King discharge during high flow.

Discharges from the Metaline Mine (Pend Oreille District/Metaline Mine Area) illustrate another application of the ratio. During low flow, the sulfate:TDS ratio reached the threshold of 20%, predicting water quality impacts from the mine. The concentration of zinc in the discharge was measured at 1180 ug/L, exceeding the state water quality standard by nearly 5-fold. During high flow, when the model would predict higher concentrations of sulfate, TDS, and metals, the ratio decreased to 17%, indicating that TDS increased at a greater rate than sulfate, resulting in a ratio less than the threshold value of 20%. However, the concentration of zinc at high flow increased to 1580 ug/L, exceeding the state water quality standard by over 5-fold. Since the Metaline Mine discharges directly into the Pend Oreille River, a downstream sample was not collected for comparison due to the disparity in flow between the mine discharge and the flow in the river.

It may be concluded from these examples that the application of the sulfate:TDS ratio has potential for identifying water quality impacts, but determining the appropriate threshold value requires further work. This study, as in the two previous studies, was limited to sampling discrete stream reaches within large mining districts. As a result, the number and distribution of samples in any district may not be adequate to completely characterize water quality throughout the district. This limitation also means that variations in water quality along the same reach, or in other streams in the district, were not accounted for in this study. The method of focused sampling also could yield water quality results that do not fit the conceptual model because they

were collected in a reach that was impacted by mine-related discharges that were not typical of the mining district as a whole. Additional sampling, to establish a reasonable sample population from which an appropriate threshold can be reasonably calculated, will be helpful to resolve this issue.

Water and Sediment Quality

A primary objective of this study was to identify receiving waters in metals mining districts that do not meet state water quality standards. Table 43 presents a summary of water quality and sediment quality impacts from the 10 mining districts included in this study. The water quality data were used to compare upstream metals concentrations against downstream concentrations. Due to the unquantified dilution of mine discharges by the receiving water, a threshold increase of twice the upstream concentration of any metal in the downstream sample is considered significant. A more robust threshold of a 10-fold increase in concentration of any metal is also included in the table. A metal may be entered in more than one column due to seasonal variations in upstream and downstream concentrations because the concentration of a metal may increase more than 2-fold in one sample event and more than 10-fold in the second sample event. This results in a metal listing in both the >2-fold increase column and in the >10-fold increase column.

The third column in Table 43 is the comparison to criteria in the state Surface Water Quality Standards, Chapter 173-201A WAC. Receiving waters impaired to the extent that they do not meet state water quality standards for protection of aquatic life are eligible for listing on an EPA-mandated report, known as the 303d list. It is the responsibility of the state to identify and then improve water quality that is impaired. Improvement can be accomplished through best management practices, clean up actions, and permitting associated with total maximum daily load calculations.

The results of this study were only compared to aquatic life criteria in the state surface water quality standards. This approach is consistent with the authors' two previous studies. It must be pointed out that other comparisons may be valid. For example, the authors do not compare these results to the human health criteria in the National Toxics Rule. Neither do we take into account potential impacts to groundwater quality by comparing to criteria in the state ground water quality standards. Finally, we do not consider the situation at some mines that have a discharge that does not appear to flow directly to surface water. Continuity between ground water and surface water can result in adverse water quality impacts that are not accounted for by assuming that impacts can only result from direct discharges.

Table 43 lists metals in sediments that exceed the Michelson (2003) recommendations. It is apparent from the table that sediment quality criteria were exceeded with greater frequency and for more metals than were water quality criteria. In addition, for sediments, more upstream exceedances were noted than occurred in the water quality samples. This is likely due to the regional extent of low grade and halo mineralization associated with major mining districts that can result in trace amounts of metals distributed over a wide area. Sediment sampling in streams is a common prospecting method in the minerals industry.

Table 43. Summary of Water and Sediment Quality Impacts Identified in Mining Districts During Present Study

NS = not sampled

Recommendations

The use of the EPA ultra low level sampling and analysis method has been affirmed by the results of this study. The low detection limits afforded by this method continue to provide water quality data at concentrations not previously attained. Future studies should employ this method. The ultra low level method is particularly useful for metals that require hardness adjustment, due to low hardness concentrations found in many of the streams and rivers where sampling occurs. The dissolved metals included in the sampling for this study, cadmium, copper, lead, arsenic, and zinc, should be carried forward for future studies. Total recoverable analyses for aluminum, iron, and mercury also should be included in future studies.

Water quality seasonality should continue to influence sampling design, although results thus far have not consistently demonstrated seasonal variations in water quality. The suggestion has been advanced that the inconsistency in seasonality may be caused by lack of winter and spring precipitation which is necessary to drive changes in metals concentrations. Due to budget timing, project sampling must begin with the low-flow sampling event. If drought conditions occur during the following winter and spring, resulting in diminished spring runoff, there is no opportunity to adjust the schedule. A better approach for seasonal sampling projects would be to begin with the spring sampling event that coincides with assured high-flow conditions, and then proceed to the low-flow sampling later in the year. In fact, this was the approach for the first study, which illustrated the role of seasonality.

It may be desirable to focus on districts that are in close proximity to each other or on a number of streams in several large districts. To accurately characterize water quality in the districts, it is desirable to optimize the timing of sampling to coincide as nearly as possible with high-flow conditions. If the mining districts that are selected for sampling are in different parts of the state and at different elevations, attempting to lay out an efficient strategy that results in sampling each district at the appropriate time is difficult.

General chemistry analyses for sulfate and total dissolved solids should be included in future studies. Including these parameters will allow continued testing of the geochemical model and progress toward the goal of fingerprinting discharges from mines. Turbidity and total suspended solids can be used as indicators for field conditions and for explaining some of the metals results. Hardness is necessary for adjusting water quality criteria. The field parameters, temperature, pH and conductivity, are easily obtained and should be part of future studies. Flow should be directly measured where possible, and estimated using best professional judgment when necessary.

The results from this study show that additional sampling should be conducted in four districts where exceedances of water quality criteria were documented.

• The Meteor Mine in the Blewett District exceeded the water quality criterion for arsenic. The downstream sample nearly exceeded the criterion and far exceeded the background concentration. Additional sampling should be focused on other mines and streams in the district.

- The Pend Oreille District covers a large area. Samples from two streams in this study and one stream in a previous study revealed exceedances of water quality criteria. Other metals showed more than 10-fold increases above background. Streams and mines in this district should be sampled in more detail.
- Milwaukee Creek in the Money Creek District exceeded water quality criteria for copper and zinc. Other mines and creeks in the district should be investigated and sampled.
- The Index District is another large mining district. Samples in the discharge from the Sunset Mine and downstream from the mine in Trout Creek exceeded the water quality criterion for copper. Other mines and streams in this district should be sampled.

For the most part, the above districts recommended for sampling based on water quality results also would be of interest based on sediment quality results. In addition to sampling in these four districts, one other district is of interest based on sediment quality.

• In the Republic District, only the EPA aluminum guideline was exceeded among the water quality criteria in Granite Creek. However, antimony, silver, and arsenic sediment quality criteria were exceeded in the sediments in Granite Creek. The presence of tailings on the creek bank at a location in close proximity to the town of Republic is cause for further investigation.

References

Betts, B. 2003. Personal communication. Washington State Department of Ecology, Olympia, WA.

Cameron, D.E. 1994. The Cannon gold mine and its surface outcrop, Wenatchee, Washington. IN Margolis, Jacob, editor, Epithermal Gold Mineralization, Wenatchee and Liberty District, Central Washington. Society of Economic Geologists Guidebook Series 20, p. 35-54.

Campbell, C.M. 1938. Report on Sunset mine, Index, Wash. Office of Ridgway R. Wilson Mining Engineer, 1 v.

Cater, F.W. and D. Crowder. 1967. Geologic map of the Holden quadrangle, Snohomish and Chelan Counties, Washington. U.S. Geological Survey Geologic Quadrangle Map GQ-646, 1 sheet, scale 1:62, 500.

CCREM. 1986. Canadian Water Quality Guidelines. Canadian Council of Resource and Environment Ministers, Ottawa, Ontario.

Cheney, E.S. and M. Rasmussen. 1996. Regional geology of the Republic area. Washington Geology, v. 24, No. 2, p. 3-7.

Church, S.E. and R. Stotelmeyer. 1984. Glacier Peak Wilderness Study Area, Washington. IN Marsh, S.P.; Kropschot, S.J.; Dickinson, R.G., editors, Wilderness Mineral Potential-- Assessment of Mineral-resource Potential in U.S. Forest Service Lands Studied 1964-1984. U.S. Geological Survey Professional Paper 1300, p. 1055-1058.

Clark, L.D. and F. Miller. 1968. Geology of the Chewelah Mountain quadrangle, Stevens County, Washington. Washington Division of Mines and Geology Geologic Map GM-5, 2 sheets, scale 1:62,500, with 6 p. text.

Cubbage, J., D. Batts, and J. Breidenbach. 1997. Creation and Analysis of Freshwater Sediment Quality Values in Washington State. Washington State Department of Ecology, Olympia, WA. Publication No. 97-323A. http://www.ecy.wa.gov/biblio/97323a.html

Culver, H.E. and W.A. Broughton. 1945. Tungsten resources of Washington. Washington Division of Geology Bulletin 34, 89 p., 23 plates.

Derkey, R.E. 1994. Metallic mineral deposits. Washington Geology, v. 22, No. 1, p. 16-18.

Derkey, R.E. 1995. A brief history of the Cannon mine. Washington Geology, v. 23, No. 1, p. 21-23.

Derkey, R.E., N.L. Joseph, and R. Lasmanis. 1990. Metal mines of Washington--Preliminary report. Washington Division of Geology and Earth Resources Open File Report 90-18, 577 p. Dings, M.G. and D.H. Whitebread. 1965. Geology and ore deposits of the Metaline zinc-lead district, Pend Oreille County, Washington. U.S. Geological Survey Professional Paper 489, 109 p., 6 plates.

EPA. 1990. Specifications and Guidance for Obtaining Contaminant-Free Sample Containers. U.S. Environmental Protection Agency. OSWER Directive #9240.0.05.

EPA. 1995. Method 1669. Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. U.S. Environmental Protection Agency. EPA 821-R-95-034.

EPA. 1996. Puget Sound Estuary Program (PSEP). Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound. U.S. Environmental Protection Agency, Region 10, Office of Puget Sound, Seattle, WA.

EPA. 2002. National Recommended Water Quality Criteria: 2002. U.S. Environmental Protection Agency. EPA 822-R-02-047.

Fulkerson, F.B. and G.A. Kingston. 1958. Mine production of gold, silver, copper, lead, and zinc in Pend Oreille and Stevens Counties, Wash., 1902-56; annual totals by mines, districts, and counties. U.S. Bureau of Mines Information Circular 7872, 51 p.

Full, R.P. and R.M. Grantham. 1968. Ore deposits of the Republic mining district, Ferry County, Washington. IN Ridge, J.D., editor, Ore Deposits of the United States, 1933-1967; The Graton-Sales volume. American Institute of Mining, Metallurgical and Petroleum Engineers, v. 2, p. 1481-1494.

Gresens, R.L. 1983. Geology of the Wenatchee and Monitor quadrangles, Chelan and Douglas Counties, Washington. Washington Division of Geology and Earth Resources Bulletin 75, 75 p., 3 plates.

Huntting, M.T. 1943. Inventory of mineral properties in Chelan County, Washington. Washington Division of Geology Report of Investigations 9, 63 p., 1 plate.

Huntting, M.T. 1956. Inventory of Washington minerals; Part II--Metallic minerals. Washington Division of Mines and Geology Bulletin 37, Part II, 2 v.

Ingersoll, C.G., P.S. Haverland, E.C. Brunsen, T.J. Canfield, F.J. Dwyer, C.E. Henke, N.E. Kemble, M.R. Mount, and R.G. Fox. 1996. Calculation and Evaluation of Sediment Effect Concentrations for the Amphipod *Hyalella azteca* and the Midge *Chironomus riparius*. J. Great Lakes Res. 22(3):602-623

Kammin, W.R., S. Cull, R. Knox, J. Ross, M. McIntosh, and D. Thomson. 1995. Labware Cleaning Protocols for the Determination of Low-Level Metals by ICP/MS. American Environmental Laboratory, v. 7, No. 9. Washington State Department of Ecology, Olympia, WA. Publication No. 95-e10.

Lasmanis, R. 1996. A historical perspective on ore formation concepts, Republic mining district, Ferry County, Washington. Washington Geology, v. 24, No. 2, p. 8-14.

Livingston, V.E., Jr. 1971. Geology and mineral resources of King County, Washington. Washington Division of Mines and Geology Bulletin 63, 200 p., 8 plates.

MacDonald, D.D., C.G. Ingersoll, and T.A. Berger. 2000. Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. Arch. Environ. Contam. Toxicol. 39:20-31.

MEL. 2003. Laboratory Users Manual, Seventh Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

Michelsen, T. 2003. Development of Freshwater Sediment Quality Values for Use in Washington State, Phase II Report. Development and Recommendation of SQVs for Freshwater Sediments in Washington State. Prep. for Washington State Department of Ecology, Toxics Cleanup Program, by Avocet Consulting, Kenmore, WA.

Miller, R.B. 1985. The ophiolitic Ingalls Complex, north-central Cascade mountains, Washington. Geological Society of America Bulletin, v. 96, No. 1, p. 27-42.

Miller, F.K. and L.D. Clark. 1975. Geology of the Chewelah-Loon Lake area, Stevens and Spokane Counties, Washington, with a section on potassium-argon ages of the plutonic rocks, by J.C. Engels. U.S. Geological Survey Professional Paper 806, 74 p., 2 plates.

Mills, J.W. 1977. Zinc and lead ore deposits in carbonate rocks, Stevens County, Washington. Washington Division of Geology and Earth Resources Bulletin 70, 171 p.

Moen, W.S. 1969. Mines and mineral deposits of Whatcom County, Washington. Washington Division of Mines and Geology Bulletin 57, 134 p., 14 plates.

National Academy of Sciences. 1973. Water Quality Criteria, 1972. EPA-R-73-033.

Ott, L.E., D. Groody, E.L. Follis, and P.L. Siems. 1986. Stratigraphy, structural geology, ore mineralogy and hydrothermal alteration at the Cannon mine, Chelan County, Washington, U.S.A. IN Macdonald, A.J., editor, Gold '86--An international symposium on the geology of gold deposits; Proceedings volume. Gold '86 [Toronto, Ont.], p. 425-435.

Park, C.F., Jr. and R.S. Cannon. 1943. Geology and ore deposits of the Metaline quadrangle, Washington. U.S. Geological Survey Professional Paper 202, 81 p., 5 plates.

Patton, T.C. and E.S. Cheney. 1971. L-D gold mine, Wenatchee, Washington – New structural interpretation and its utilization in future exploration. Society of Mining Engineers of AIME Transactions, v. 250, No. 1, p. 6-11.

Patty, E.N. 1921. The metal mines of Washington. Washington Geological Survey Bulletin 23, 366 p.

Persaud, D., R. Jaagumagi, and A. Hayton. 1993. Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario. Ontario Ministry of Environment and Energy. ISBM 0-7729-9248-7.

Raforth, R.L., A. Johnson, and D.K. Norman. 2000. Screening Level Investigation of Water and Sediment Quality of Creeks in Ten Eastern Washington Mining Districts, with Emphasis on Metals. Washington State Department of Ecology, Olympia, WA. Publication No. 00-03-004. http://www.ecy.wa.gov/biblio/0003004.html

Raforth, R.L., D.K. Norman, and A. Johnson. 2002. Second Screening Investigation of Water and Sediment Quality of Creeks in Ten Washington Mining Districts, with Emphasis on Metals. Washington State Department of Ecology, Olympia, WA. Publication No. 02-03-024. http://www.ecy.wa.gov/biblio/0203024.html

Staatz, M.H. and R.C. Pearson. 1990. The Republic gold district, Ferry County, Washington. IN Epithermal gold deposits--Part I. U.S. Geological Survey Bulletin 1857-H, p. H14-H20.

Tabor, R.W., V.A. Frizzell, Jr., D.B. Booth, R.B. Waitt, J.T. Whetten, and R.E. Zartman. 1993. Geologic map of the Skykomish River 30- by 60-minute quadrangle, Washington. U.S. Geological Survey Miscellaneous Investigations Series Map I-1963, 1 sheet, scale 1:100,000, with 42 p. text

Tabor, R.W., R.A. Haugerud, D.B. Booth, and E.H. Brown. 1994. Preliminary geologic map of the Mount Baker 30- by 60-minute quadrangle, Washington. U.S. Geological Survey Open-File Report 94-403, 55 p., 2 plates.

Wolff, F.E., D.T. McKay, Jr., and D.K. Norman. 2001. Inactive and abandoned mine lands – Apex mine, Money Creek mining district, King County, Washington. Washington Division of Geology and Earth Resources Open File Report 2001-2, 8 p.

Wolff, F.E., D.T. McKay, Jr., and D.K. Norman. 2002. Inactive and abandoned mine lands – Sunset mine, Snohomish County, Washington. Washington Division of Geology and Earth Resources Open File Report 2002-4, 8 p.

Wolff, F.E., D.T. McKay, Jr., and D.K. Norman. 2003. Inactive and abandoned mine lands – United Copper Group Mines, Chewelah Mining District, Stevens County, Washington. Washington Division of Geology and Earth Resources Open File Report 2003-17, 17 p.

Woodhouse, P.R., editor and compiler; D. Jacobson, B. Petersen, V. Pisoni. 1996. Hard rock mines of the west central Cascades. Northwest Underground Explorations [Seattle, Wash.], 233 p.

Appendices

- A. Metals Criteria Formulas
- B. Results on Field Blanks for Water Samples
- C. Results on Field Replicates for Water Samples
- D. Results on Laboratory Splits for Metals in Water Samples
- E. Results on Laboratory Splits for General Chemistry
- F. Results on Field Replicates for Sediment Samples
- G. Results on Laboratory Splits for Sediment Samples
- H. Results on Field Measurements and General Chemistry for Water Samples
- I. Metals Concentrations in Water Samples
- J. Metals Concentrations in Sediment Samples
- K. Key for Water and Sediment Samples
- L. List of Minerals Referred to in this Report
- M. Glossary of Geologic and Mining Terms

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Appendix A. Metals Criteria Formulas

Washington State surface water quality standards for cadmium, lead, silver, and zinc are hardness dependent and can be calculated by the following formulas (WAC 173-201A):

Cadmium - acute = $(1.136672 - [(ln hardness)(0.041838)])(e^{(1.128[ln(hardness)]-3.828)})$

Cadmium - chronic = $(1.101672$ -[(ln hardness) (0.041838)])($e^{(0.7852[ln(hardness)]-3.490)}$)

Copper - acute = $(0.960)(e^{(0.9422[ln(hardness)]-1.464)})$

Copper - chronic = $(0.960)(e^{(0.8545[\ln(\text{hardness})]-1.465)})$

Lead - acute = $(1.46203 - [(ln hardness)(0.145712)])(e^{(1.273[ln(hardness)]-1.460)})$

Lead - chronic = $(1.46203$ -[(ln hardness) (0.145712)])($e^{(1.273[ln(hardness)]-4.705)}$)

Silver - acute = $(0.85)(e^{(1.72[\ln(\text{ hardness})] - 6.52)})$

Zinc - acute = $(0.978)(e^{(0.8473[ln(hardness)]+0.8604)})$

Zinc - chronic = $(0.986)(e^{(0.8473[\ln(\text{ hardness})]+0.7614)})$

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Appendix B. Results on Field Blank for Water Samples (μ g/L)

na = not analyzed

 $U = not detected at or above reported value$

^a0.5 L Teflon bottles precleaned and filled with blank water by Manchester Laboratory and acidified in the field. **The Teflon bottles cleaned and filled as above, then filtered and acidified in the field**

Appendix C. Results on Field Replicates for Water Samples

Detections highlighted in BOLD

RPD = relative percent difference (range as percent of duplicate mean)

 $UI = not detected at or above the reported estimated value$

 $U = not detected at or above reported value$

Appendix C (continued).

Detections highlighted in BOLD

RPD = relative percent difference (range as percent of duplicate mean)

 $UI = not detected at or above the reported estimated value$

 $U = not detected at or above reported value$

Appendix D. Results on Laboratory Splits for Metals in Water Samples (ug/L)

Detections highlighted in BOLD

RPD = relative percent difference (range as percent of duplicate mean)

 $U = not detected at or above reported value$

Appendix E. Results on Laboratory Splits for General Chemistry (mg/L)

Detections highlighted in BOLD

RPD = relative percent difference (range as percent of duplicate mean)

 $UI = not detected at or above the reported estimated value$

 $U = not detected at or above reported value$

Appendix F. Results on Field Replicates for Sediment Samples (mg/Kg, dry)

Detections highlighted in BOLD

RPD = relative percent difference (range as percent of duplicate mean)

 $U = not detected at or above reported value$

Appendix G. Results on Laboratory Splits for Sediment Samples (mg/Kg, dry)

Detections highlighted in BOLD

RPD = relative percent difference (range as percent of duplicate mean)

 $U = not detected at or above reported value$

Appendix H. Results on Field Measurements and General Chemistry for Water Samples

Detections highlighted in BOLD

 $U = not detected at or above the reported result.$

J = estimated result

UJ = estimated value below the detection limit

NM = not measured
Appendix H (continued).

Detections highlighted in BOLD

 $U = not detected at or above the reported result.$

J = estimated result

 $\mathbf{U}\mathbf{J} =$ estimated value below the detection limit

NM = not measured

Appendix I. Metals Concentrations in Water Samples (µg/L)

Detections highlighted in BOLD

* = exceeds water quality criterion

 $U = not detected at or above the reported result.$

 ${\bf J} =$ estimated result

UJ = estimated value below the detection limit

Appendix I (continued).

Detections highlighted in BOLD

* = exceeds water quality criterion

 $U = not detected at or above the reported result.$

J = estimated result

UJ = estimated value below the detection limit

Appendix J. Metals Concentrations in Sediment Samples (mg/Kg, dry)

Detections highlighted in BOLD

* = exceeds sediment quality guideline

 $U = not detected at or above the reported result.$

J = estimated result

Appendix J (continued).

Detections highlighted in BOLD

* = exceeds sediment quality guideline

 $U = not detected at or above the reported result.$

 $\mathbf{J} =$ estimated result

NS = no sample

Appendix L. List Of Minerals Referred To In This Report

Anglesite PbSO4 ---- 68.32% Pb (MW = 303.26 gm) Argentite Ag2S ---- 87.06% Ag (MW = 247.80 gm) Arsenopyrite FeAsS ---- 46.01% As (MW = 162.83 gm) Azurite Cu3(CO3)2(OH)2 ---- 55.31% Cu (MW = 344.67 gm) Biotite $K(Mg,Fe++)3(Al,Fe++)+Si3O10(OH,F)2$ Calcite CaCO3 ---- 40.04% Ca (MW = 100.09 gm) Cerussite PbCO3 ---- 77.54% Pb (MW = 267.21 gm) Chalcocite Cu2S ---- 79.85% Cu (MW = 159.16 gm) Chalcopyrite CuFeS2 ---- 34.63% Cu (MW = 183.53 gm) Dolomite CaMg(CO3)2 ---- 21.73% Ca (MW = 184.40 gm) Electrum ---- an alloy of gold with silver Epidote Ca2(Fe+++,Al)3(SiO4)3(OH) = Ca2(Fe,Al)Al2(SiO4)(Si2O7)O(OH) Fluorite CaF2 ---- 48.67% F (MW = 78.07 gm) Galena PbS ---- 86.60% Pb (MW = 239.27 gm) Hematite Fe2O3 ---- 69.94% Fe (MW = 159.69 gm) Limonite Fe +++ $O(OH)$ Magnetite Fe++Fe+++2O4 ---- 72.36% Fe (MW = 231.54 gm) Malachite Cu2(CO3)(OH)2 ---- 57.48% Cu (MW = 221.12 gm) Molybdenite MoS2 ---- 59.94% Mo (MW = 160.07 gm) Naumannite Ag2Se ---- 26.79% Se (MW = 294.70 gm) Polybasite (Ag,Cu)16Sb2S11 Pyrargyrite Ag3SbS3 ---- 22.48% Sb (MW = 541.55 gm) Pyrite FeS2 ---- 46.55% Fe (MW = 119.98 gm) Pyrrhotite Fe(1-x)S(x=0-0.17) ---- 62.33% Fe (MW = 85.12 gm) Quartz SiO2 ---- 46.74% Si (MW = 60.08 gm) Realgar AsS ---- 70.03% As (MW = 106.99 gm) Scheelite CaWO4 ---- 63.85% W (MW = 287.93 gm) Sericite (Muscovite) KAl2(Si3Al)O10(OH,F)2 ---- 9.82% K (MW = 398.31 gm) Sphalerite (Zn,Fe)S ---- 67.10% Zn (MW = 97.46 gm) Stephanite Ag5SbS4 ---- 68.33% Ag (MW = 789.36 gm) Stibnite Sb2S3 ---- 71.68% Sb (MW = 339.70 gm) Tellurides are a combination of a metal and tellurium (such as Hessite, Telluric Silver) Ag2Te Tetrahedrite (Cu,Fe)12Sb4S13 Umangite Cu3Se2 ---- 54.69% Cu (MW = 348.56 gm)

Appendix M. Glossary of Geologic and Mining Terms

adit - A horizontal passage from the surface for the working or unwatering of a mine .

amalgamation - The process by which mercury is alloyed with some other metal to produce an amalgam.

amphibolite facies - An assemblage of minerals formed during regional metamorphism at moderate to high pressures between 450 and 700º C. Amphibolite is a faintly foliated metamorphic rock developed during regional metamorphism. Composed mainly of hornblende and plagioclase feldspars.

argillite - A compact rock, derived from mudstone (claystone or siltstone) or shale that has undergone a somewhat higher degree of induration (rendered hard).

arkose - A detrital sedimentary rock formed by cementation of individual grains of sand size and predominantly composed of quartz and feldspar. Derived from disintegration of granite.

arrastre – A circular rock-lined pit in which broken ore is pulverized by stones attached to horizontal poles fastened in a central pillar and dragged around the pit.

breccia - Clastic rock made up of angular fragments of such size that an appreciable percentage of rock volume consists of particles of granule size or larger.

carbonate - A mineral formed by a combination of complex ion $(CO_3)^2$ with a positive ion. Common example: calcite, CaCO₃.

chert - Granular cryptocrystalline silica, similar to flint but usually light in color. Occurs as compact massive rock or as nodules.

clastic- Being or pertaining to a sedimentary rock composed primarily from fragments of preexisting rocks or fossils.

crosscut - A small passageway driven at an angle to the main entry of a mine, to connect it with a parallel entry, an air course, or across an ore body to test its width and value.

dike - A discordant pluton that is substantially wider than it is thick. Dikes are often steeply inclined or nearly vertical. See also "sill."

diorite - Coarse-grained igneous rock with a composition of andesite (no quartz or orthoclase), composed of 75 percent plagioclase feldspars and balance ferromagnesian silicates.

drift - A horizontal passage underground that follows the vein.

dumps - A place where the ore taken from a mine is tipped. Also a spoil heap at the surface of a mine.

epithermal - Said of a hydrothermal mineral deposit formed within about 1 kilometer of the earth's surface and in the temperature range of 50-200ºC.

fault - Surface of rock rupture along which has been differential movement.

flotation - The method of mineral separation in which a froth created in water by a variety of reagents floats some finely crushed minerals , whereas other minerals sink.

graben - Elongated, trench-like, structural form bounded by parallel normal faults created when block that forms trench floors moves downward relative to blocks that form sides.

granodiorite - Coarse-grained igneous rock intermediate in composition between granite and diorite.

graywacke - A variety of sandstone generally characterized by hardness, dark color, and angular grains of quartz, feldspar, and small rock fragments set in a matrix of clay-sized particles. Also called lithic sandstone.

greenschist facies - Assemblage of minerals formed between 150 and 250ºC during regional metamorphism. Greenschist - schist characterized by green color. Product of regional metamorphism. (Green color is imparted by mineral chlorite.)

hydrothermal alteration - The chemical metamorphism of preexisting rocks that is caused by the action of hot water.

igneous rock - Aggregate of interlocking silicate minerals formed by cooling and solidification of magma.

limestone - Sedimentary rock composed largely of mineral calcite, CaCO3, formed by either organic or inorganic processes. Most limestones have clastic texture, but nonclastic, particularly crystalline, textures are common. Carbonate rocks, limestone and dolomite, constitute an estimated 12 to 22 percent of sedimentary rocks exposed above sea level.

massive sulfide - Any mass of unusually abundant metallic sulfide minerals.

metamorphic rock - "Changed-form rock." Any rock changed in texture or composition by heat, pressure, or chemically active fluids after original formation.

mill - Generally the crushing, grinding, and processing of ore to extract the mineral or metal of interest.

mine - An excavation for the purpose of extracting minerals.

mining district - A section of country usually designated by name, having described or understood boundaries within which mineral is found and which is worked under rules and regulations prescribed by the miners therein.

Mississippi Valley type zinc-lead deposit - A stratabound deposit of lead and/or zinc minerals in carbonate rocks. These deposits characteristically have relative simple mineralogy. These occur as veins and replacement bodies, are at moderate to shallow depths, show little post-ore deformation, are marginal to sedimentary basins, and are without an obvious source of the mineralization.

open pit - Surficial mining, in which the valuable rock is exposed by removal of overburden.

ore - The naturally occurring material from which a mineral or minerals or metal of economic value can be extracted at a reasonable profit.

placer - A concentration of relatively heavy and resistant minerals in stream or beach deposits; two examples are some deposits of gold and of diamonds.

pluton - A body of igneous rock formed beneath the earth's surface by consolidation from magma. Sometimes extended to include bodies formed beneath the surface by metasomatic replacement of older rock.

portal - A mouth of an adit or tunnel.

propylitic alteration - A hydrothermal alteration or process involving the formation of an altered andesite resembling a greenstone and containing calcite, chlorite, epidote, serpentine, quartz, pyrite, and iron oxides (a propylite).

sedimentary rock - Rock formed from accumulations of sediment, which may consist of rock fragments of various sizes, remains or products of animals or plants, products of chemical action or of evaporation, or mixtures of these. Stratification is the single most characteristic feature of sedimentary rocks, which cover about 75 percent of land area.

sericitic alteration - A type of hydrothermal alteration involving the alteration to or placement by sericite muscovite.

shaft - A vertical or inclined excavation through which a mine is worked.

sill - A concordant pluton that is substantially wider than it is thick. Sills form within a few kilometers of the earth's surface. See also "dike."

stamp mill - An apparatus in which rock is crushed by descending pestles (stamps).

stocks - Discordant pluton that increases in size downward, has no determinable floor, and shows area of surface exposure less than 100 km^2 .

stockwork - A mineral deposit consisting of a three-dimensional network of planar to irregular veinlets closely spaced so that a whole mass can be mined.

tailings - The portions of washed or milled ore that are regarded as too poor to be treated further, as distinguished from the concentrates or material of value.

tuff - Rock consolidated from volcanic ash.

volcaniclastic - Pertaining to a clastic rock containing volcanic material in whatever proportion, and without regard to its origin or environment.

volcanics - Pertaining to the activities, structures, or rock types of a volcano.