# Second Screening Investigation of Water and Sediment Quality in Creeks in Washington Mining Districts

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Quality Assurance Project Plan

by
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Environmental Assessment Program, Watershed Ecology Section
&
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*draft completed July 11, 2000 and reviewed by signers prior to field work

## Project Description

The purpose of this project is to obtain water and sediment quality data on streams draining selected metals mining districts in eastern and western Washington. This study is needed to fill a data gap for characterization of discharges from abandoned metals mines, waste rock dumps, or tailings found in inactive or abandoned mining districts. The work will be conducted jointly by the Washington State Department of Ecology (Ecology) Central Regional Office (CRO) and Environmental Assessment Program (EAP), and with the Department of Natural Resources (DNR). Water draining from some individual mines and tailings may be opportunistically sampled, but sampling of individual mines is not a priority.

The emphasis will be on ultra-clean metals analyses by the Ecology Manchester Environmental Laboratory along with selected general chemistry and field parameters. At most sites, sampling will occur during low flow conditions (August 2000 for high altitude sites, late September/early October 2000 otherwise) and re-sampled during high flow (May/June 2001) to account for seasonality in water quality. Sediment sampling would be conducted during low flow conditions only. Due to their remote location, some sites may only be accessible for one round of water quality sampling.

This project is a continuation of the recently published "Ten Mines Study" (Raforth et al., 2000). Primarily, this project would focus on extending stream and sediment sampling to additional mining districts not covered in the original study, including some located in the Cascade Range at high altitude. The plan is to sample an additional ten mining districts, although a final decision on which districts to sample has not been made.

This project would implement sampling and parameter recommendations discussed in the Ten Mines report, such as investigating the sulfate:TDS (total dissolved solids) ratio for fingerprinting mine impacts. The new study would also support a cooperative site ranking process that is being negotiated between Ecology's Toxics Cleanup Program and EPA to identify and classify mining impacts. Data obtained in this project would support watershed planning through identification of water quality impaired streams.

The general approach will be to establish sampling sites in the largest and nearest potentially impacted stream. One site will be located upstream of the mining district, with a second sampling site in the same stream downstream of the mining district. Water samples will be collected using the EPA (1995) ultra-clean sampling procedures for metals. The metals to be analyzed in filtered water samples are arsenic, lead, cadmium, copper, and zinc. Mercury, aluminum, and iron will be analyzed in whole water samples.

Conventional water quality parameters will include hardness, TDS, total suspended solids (TSS), sulfate, and turbidity. Temperature, pH, conductivity, and flow will be measured in the field. Composite sediment samples will be collected from each site and analyzed for grain size, EPA priority pollutant metals (Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Tl, and Zn), iron, aluminum, and manganese. Fine-grain material will be preferentially sampled.

Results will be compared to state water quality standards for aquatic life (WAC 173-201A), EPA water quality criteria (iron and aluminum, EPA, 1999), and to guidelines for freshwater sediments (e.g., Persaud et al., 1993; Cubbage et al., 1997).

Table 1 shows the number of samples to be collected and the cost of laboratory analysis.

## Schedule

~~(exact dates to be determined)~~

August 2000.....Low flow sampling (high altitude sites)
Sept.- October 2000.....Low flow sampling (other sites)
January 2001.....Laboratory analyses completed
February 2001.....Progress Report
May - June 2001.....High flow sampling (all sites)
September 2001.....Laboratory analyses completed
March 2002.....Draft report
July 2002.....Final report
September 2002.....Data entered into EIM

## Project Organization

Project Lead - Bob Raforth (509/457-7113)
Technical Assistance - Art Johnson (360/407-6766)
DNR Cooperator - Dave Norman (360/902-1439)
Manchester Laboratory Director - Stuart Magoon (360/871-8801)
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## Data Quality Objectives

Precision and Bias

The data quality objective for accuracy will be +/- 20% (bias target of 10% and precision target 5%RSD (95% C.I. based on 2 standard deviations or 10% RSD).

Table 1. Number of Samples and Laboratory Cost Estimate

| Sample Type | Analysis | No. of Samples* | Sampling Periods** | Total Samples | Cost per Sample | Cost Subtotals |
|---|---|---|---|---|---|---|
| 1. WATER | | | | | | |
| Field Samples | Diss. As,Cd,Cu,Pb,Zn | 20 | 2 | 40 | 204 | 8160 |
| " | Tot. Rec. Al, Fe | 20 | 2 | 40 | 38 | 1520 |
| " | Total Hg | 20 | 2 | 40 | 48 | 1920 |
| " | Hardness | 20 | 2 | 40 | 12 | 480 |
| " | TDS | 20 | 2 | 40 | 10 | 400 |
| " | TSS | 20 | 2 | 40 | 10 | 400 |
| " | Sulfate | 20 | 2 | 40 | 12 | 480 |
| " | Turbidity | 20 | 2 | 40 | 7 | 280 |
| Replicate Samples | Diss. As,Cd,Cu,Pb,Zn | 1 | 3 | 3 | 204 | 612 |
| " | Tot. Rec. Al, Fe | 1 | 3 | 3 | 38 | 114 |
| " | Total Hg | 1 | 3 | 3 | 48 | 144 |
| " | Hardness | 1 | 3 | 3 | 12 | 36 |
| " | TDS | 1 | 3 | 3 | 10 | 30 |
| " | TSS | 1 | 3 | 3 | 10 | 30 |
| " | Sulfate | 1 | 3 | 3 | 12 | 36 |
| " | Turbidity | 1 | 3 | 3 | 7 | 21 |
| Filter Blanks | Diss. As,Cd,Cu,Pb,Zn | 1 | 2 | 2 | 204 | 408 |
| Bottle Blanks | Tot. Rec. Al, Fe | 1 | 2 | 2 | 38 | 76 |
| " | Total Hg | 1 | 2 | 2 | 48 | 96 |
| | | | | +0.45 um filters @$21 ea = | | 945 |
| | | | | +500 mL teflon bottles @$14 ea = | | 1260 |
| | | | | +teflon acid vials @ $7 ea = | | 630 |
| 2. SEDIMENT | | | | | | |
| Field Samples | Priority Metals,Al,Fe,Mn | 20 | 1 | 20 | 228 | 4560 |
| " | Grain size | 20 | 1 | 20 | 100 | 2000 |
| Dup. Matrix Spikes | Priority Metals,Al,Fe,Mn | 2 | 1 | 2 | 228 | 456 |
| | | | | TOTAL LAB COST = | | $ 25,094 |

*10 mining districts, 2 sampling sites/district

**low flow and high flow (2 low flow replicate samples, August and Sept.-Oct.)

Limits of Detection

Table 2 shows the state water quality standards and EPA criteria the metals data will be compared to. The hardness-dependent values for dissolved cadmium, copper, lead, and zinc are the lowest that might reasonably be encountered, based on results from the "Ten Mines Study". The limits of detection required for determining exceedances of standards or criteria are set at a factor of 10 lower. Detection limits are not an issue for comparing metals concentrations in sediment samples to sediment quality guidelines, previously mentioned.

Table 2. Detection Limit Requirements for Metals in Water (ug/L)

| Metal | Chronic State Standard or EPA Chronic Criterion | Required Limit of Detection[c] |
|---|---|---|
| Arsenic - dissolved | 190 | 19 |
| Lead - dissolved | 0.19[a] | 0.019 |
| Cadmium - dissolved | 0.19[a] | 0.019 |
| Copper - dissolved | 1.59[a] | 0.16 |
| Zinc - dissolved | 15[a] | 1.5 |
| Mercury - total | 0.012 | 0.001 |
| Aluminum - tot. recov. | 87[b] | 8.7 |
| Iron - total recoverable | 1,000[b] | 100 |

[a]at a hardness of 10 mg/L

[b]EPA criterion

[c]standard or criteria divided by 10

Representativeness

The sampling design is intended to give results that are representative of water and sediment quality in the areas studied, within the limits of the available funding. Measures taken in the interest of obtaining representative data include locating sampling sites sufficiently far downstream from sources to allow for complete mixing and a sampling plan that accounts for seasonality in water quality. Sediment samples are being collected as composites to improve representativeness. Because only a single water sample will be collected for most sites for each sampling period, the results may not represent the range of water quality conditions that occur during high flow.

Completeness

The amount of useable data obtained will be maximized by careful planning of field work, following EPA sampling guidance, and taking care in packaging and transport of samples. Manchester will save excess sample for 60 days from the time the data is sent to the project lead to give time for its review.

Comparability

Sampling, quality assurance, and analytical methods are the same as in the previous "Ten Mines Study".

## Sampling Methods

Sampling methods for metals in water will follow EPA Method 1669 and for sediment will be consistent with PSEP protocols (EPA, 1996). Chain of custody will be maintained.

All water samples will be collected as simple grab samples. Water samples for metals analysis will be collected directly into pre-cleaned 500 mL Teflon bottles. Samples for dissolved metals will be vacuum-filtered in the field through a disposable 0.45 μm cellulose nitrate filter (#450-0045, type S). Non-talc, disposable gloves will be worn during the filtering procedure. The filtrate will be transferred to a clean Teflon bottle and preserved to pH <2 with sub-boiled 1:1 nitric acid, carried in small Teflon vials, one per sample. Unfiltered water samples for aluminum, iron, and mercury will be preserved in the same manner. Depending on the field pH reading, the amount of acid used will range from approximately 2 mL (acidic or neutral pH) to 5 mL(basic).

Teflon sample bottles will be supplied by Manchester, cleaned as described in Kammin et al. (1995), and sealed in plastic bags. Each metals sample will be placed in double plastic bags and all samples will be held on ice for transport to Manchester Laboratory. General chemistry samples will be collected in 1 liter polyethylene bottles. Sample containers and preservation for general water quality parameters are described in MEL (1994).

Sediment samples will be composites of multiple grabs taken with stainless steel scoops and homogenized in the field in stainless steel bowls. Sampling equipment will be cleaned by

washing with Liquinox detergent and sequential rinses with tap water, dilute nitric acid, and DI water. The homogenate will be 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.

Field measurements for pH and temperature will be obtained with an Orion Model 250A meter; field conductivity will be measured with an Orion Model 120 conductivity meter. The pH meter will be calibrated daily. Streamflow measurements will be made with a Marsh-McBirney flow meter and top-setting rod. Station positions will be recorded from a hand-held GPS.

## Laboratory Methods

Sample analysis will be conducted by Manchester Laboratory, except for grain size which will be done by a contract laboratory selected by Manchester.

Water samples will be analyzed for dissolved arsenic, lead, cadmium, copper, and zinc by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) following EPA method 200.8. Aluminum and iron will be determined by ICP, EPA Method 200.7. Mercury will be analyzed by EPA method 245.7, modified for Cold Vapor Atomic Absorption (CVAA). Analysis for general water quality parameters will follow routine methods described in MEL (1994).

Table 3 shows Manchester's reporting limits for the above metals. These reporting limits meet the data quality objectives for this project (Table 2).

Table 3. Manchester Reporting Limits for Metals in Water (ug/L)

| Metal | Reporting Limit | Method |
|---|---|---|
| Arsenic | 0.2 | ICP/MS |
| Lead | 0.02 | ICP/MS |
| Cadmium | 0.02 | ICP/MS |
| Copper | 0.05 | ICP/MS |
| Zinc | 0.4 | ICP/MS |
| Mercury | 0.002 | CVAA |
| Aluminum | 20 | ICP |
| Iron | 20 | ICP |

Metals analysis of sediment samples will be by ICP according to EPA method 200.7 (aluminum, iron, manganese, zinc, chromium, copper, lead, nickel, cadmium, silver, beryllium, antimony); Graphite Furnace Atomic Absorption (GFAA) according to EPA methods 206.2 (arsenic), 270.2 (selenium), and 279.2 (thallium); and CVAA according to EPA method 245.5 (mercury). Metals other than mercury will be digested with nitric and hydrochloric acids by EPA method 3050. The mercury digestion is described in method 245.5. Grain size will be determined by sieve and pipette using the Puget Sound Estuary Program method (EPA, 1996).

## Quality Control Procedures

Field QC samples for water will include bottle blanks, filter blanks, and replicate samples. No field QC samples will be collected for sediment.

The field blanks will be used to check for metals contamination arising from sample containers or the filtration procedure. Bottle blanks will consist of 500 mL Teflon bottles cleaned and filled with de-ionized (DI) water at Manchester Laboratory, as previously described. Filter blanks were prepared by filtering the contents of a DI-filled Teflon bottle. One pair of bottle and filter blanks each will be prepared for low flow and high flow field work.

The total variability (field + laboratory) of the metals and conventional water quality data for this project will be assessed by collecting selected samples in replicate. The replicates will consist of two separate sets of samples collected approximately five minutes apart. One pair of replicates each will be collected during the August, September-October, and May-June sample collections.

Laboratory QC samples for metals to be analyzed with each set of water samples will include a duplicate sample analysis (lab split), standard reference material (SRM) certified for low metals concentrations in river water (SLRS-3 or equivalent), a laboratory control sample (LCS), and a method blank.

Laboratory QC samples for metals to be analyzed with each set of sediment samples will include an LCS, a duplicate sample analysis (lab split), a matrix spike and spike duplicate, and a method blank.

## Data Assessment Procedures and Reporting

Manchester's SOP for data reduction, review, and reporting will meet the needs of this project. Each laboratory unit assembles data packages consisting of raw data from the analyses of the samples, copies of the pertinent logbook sheets, QA/QC data, and final reports of data entered into LIMS. These data packages are subjected to a data verification and quality assurance review by another analyst familiar with the procedure.

Reviewers use *US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review* February, 1994 and *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, October, 1999.

The following additional information will be reported for the metals data: 1) the name, source, and certified values for SRMs and LCSs analyzed; 2) the metals concentrations measured in the SRM and LCS (in addition to percent recovery); and 3) the spiking levels used in matrix spikes.

The project lead will prepare a draft report of the overall study by March 2002. The report will contain:

- a map of the study area showing sampling sites
- latitude/longitude and other location information for each sampling site
- descriptions of field and laboratory methods
- a discussion of data quality, estimates of precision and bias, and the significance of any problems encountered in the analyses
- summary tables of the metals and ancillary data
- an evaluation of significant findings with respect to exceedances of standards and guidelines, differences within and between mining districts, seasonality, sulfate:TDS ratios, comparison with the previous mine study, and additional data interpretation as appropriate
- recommendations for follow-up work if warranted.

Due to the screening-level nature of this investigation, with only one upstream and one downstream sample typically being collected for each site in the fall and again in the spring (water only), statistical testing for significant differences will not be possible. Identification of sites impacted by mining will be made by a simple comparison of upstream and downstream values, taking the estimates of field and laboratory variability from replicate and duplicate samples into account.

A final report will be prepared after receiving review comments from CRO, DNR, and EAP. The goal is to have the revised final report completed on or before July 2002. The data will be entered into Ecology's Environmental Information Management (EIM) system by September 2002.

## References

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