Levels and Sources of Arsenic in the Similkameen River

Quality Assurance Project Plan

by
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Environmental Investigations and Laboratory Services Program
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Background

The Similkameen River is on the 303(d) list for exceeding EPA National Toxics Rule (NTR) human health criteria for inorganic arsenic. The NTR criteria not to be exceeded are 0.14 ug/L for consumption of aquatic organisms and 0.018 ug/L for consumption of both water and organisms. This listing is based on concentrations of 2.9 – 4.8 ug/L total recoverable arsenic measured during a 1995-96 screening survey by the Washington State Dept. of Ecology (Ecology) Environmental Assessment Program (EAP) (Johnson, 1997). The EPA drinking water standard will be lowered from 50 ug/L to 5 ug/L in early 2001. State water quality standards for protection of aquatic life, 190 – 360 ug/L (dissolved), have not been approached in the Similkameen.

It is likely that most Washington rivers have naturally occurring arsenic levels that exceed the very low NTR criteria. However, based on statewide monitoring done by EAP, arsenic concentrations in the Similkameen are higher than the 1 ug/L or less typical of other major rivers.

The major known source of arsenic to the Similkameen is mine tailings in British Columbia (B.C.) between Hedley and the U.S. border (Stewart, 1998; Pommen, 1998). The B.C. Ministry of Environment, Lands & Parks and Environment Canada monitor water quality jointly at a station on the Similkameen River @ Chopaka Bridge (federal site no. BC08NL0005), approximately 11 miles above the border. Results have shown that total recoverable arsenic concentrations peak during spring freshets (Figure 1). Historically, concentrations have reached 45 ug/L. In recent years (1997–99) the concentrations reported by B.C. have averaged 2 ug/L, with up to 20 ug/L in the spring.

B.C. analyzes total recoverable and extractable* arsenic at their routine monitoring station on the Similkameen. In 1999 they began monitoring dissolved arsenic during the spring freshets.

Ambient monitoring by EAP near the mouth of the river at Oroville during 1995-97 showed an average total recoverable arsenic concentration of 5.6 ug/L, with a maximum of 22 ug/L (Table 1). Dissolved arsenic was not analyzed and monitoring was discontinued after 1997. Because of the limited sampling done by Ecology and lack of correspondence with sampling dates in B.C., it is not possible to determine if arsenic concentrations increase or decrease downstream of the border.

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* Extractable metals samples are collected unfiltered and preserved in the field to about pH 2 with nitric acid. The sample is analyzed by ICP-MS without further digestion. The results are thought to represent the fraction of metals that are bio-available.

Table 1. Arsenic Concentrations in the Similkameen River @ Oroville (ug/L)
Ecology Ambient Monitoring Station 49B070

Sampling Date	Tot. Rec. Arsenic
12/11/95	22
2/12/96	1.9
4/15/96	3.6
6/11/96	6.3
8/13/96	3.8
10/15/96	2.8
12/10/96	1.9
4/15/97	2.0
6/10/97	8.3
8/12/97	4.2

The Colville Confederated Tribes and Ecology Central Regional Office (CRO) have requested that EAP investigate arsenic levels in the Similkameen River, as a first step in a TMDL. The objectives of this study will be to:

- Document the current extent and frequency of exceedances of NTR criteria at the international border.
- Determine if arsenic concentrations increase or decrease between the border and mouth of the river, including seasonal variation.
- Identify all known and other potential arsenic sources to the river within Washington and assess their impact on arsenic levels in the river.
- Establish a pollutant load allocation for all known sources and a safety margin that would bring the waterbody into compliance with water quality standards.

Study Plan

1. Routine Monitoring

The EAP Freshwater Monitoring Unit (FMU) will collect monthly samples for total recoverable and dissolved arsenic at their Similkameen @ Oroville station (49B070) and at the Similkameen River @ Chopaka Bridge B.C. (Figure 2). Comparability of the arsenic data will be improved by having the upstream and downstream samples collected by the same field person, on or about the same date, and analyzed by the same method

and laboratory, rather than relying on the B.C. monitoring program for upstream arsenic data.

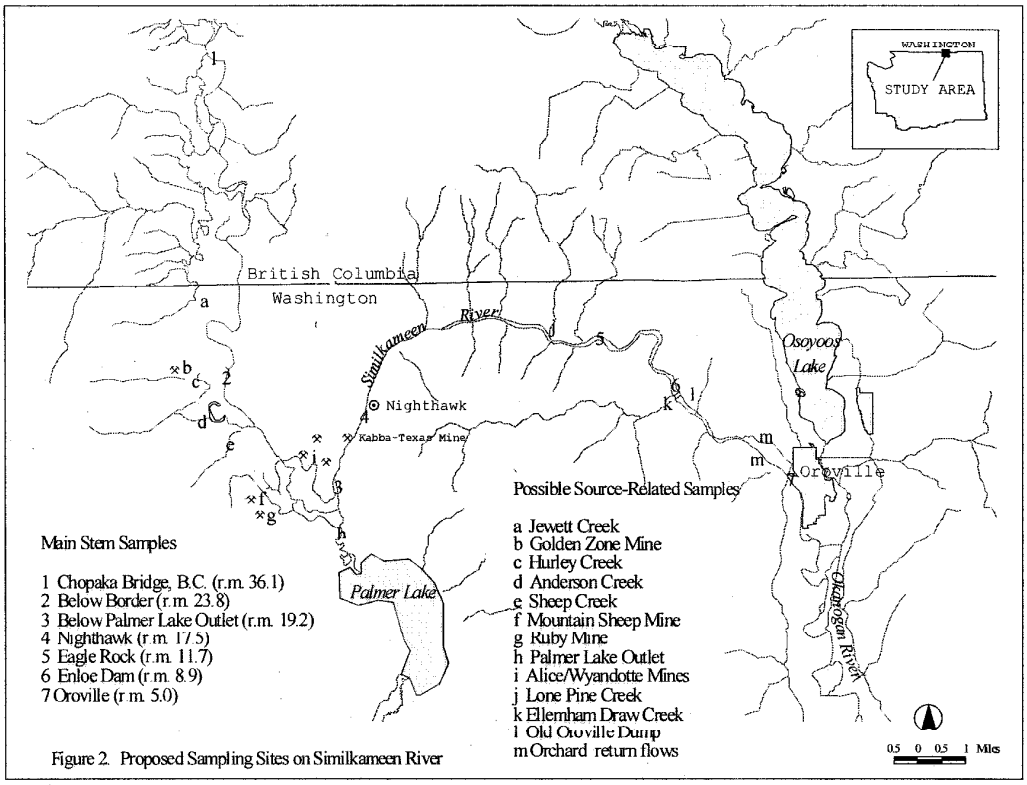

Figure 2. Proposed Sampling Sites on Similkameen River

FMU began arsenic monitoring in May 2000 and will continue through June 2001 in order to cover two seasonal peaks for arsenic. Hardness and other FMU routine water quality parameters* are being analyzed for both stations. Flow data will be obtained from the EAP Stream Hydrology Unit and B.C. Ministry of Environment, Lands & Parks.

2. Intensive Surveys

The EAP Watershed Ecology Section (WES) will conduct two intensive surveys to identify arsenic sources within the Washington portion of the watershed. More detailed data will also be obtained on the main stem, to identify reaches gaining or losing arsenic in the water column. One survey will be conducted during low-flow in October 2000, the other during high flow in May or June 2001.

*conductivity, D.O., pH, temperature, TSS, turbidity, fecal coliform bacteria, soluble reactive phosphorus, total phosphorus, ammonia, nitrate+nitrite, total nitrogen

Potential arsenic sources in Washington include tributaries, abandoned mines, orchards which historically used arsenical pesticides, and waste dumps. The locations of these types of sites will be identified with the help of CRO and in reconnaissance during the low flow survey.

A number of creeks and intermittent streams drain an area of abandoned mines along the right bank (facing downstream) of the upper river between the border and Nighthawk. The flow from many of these may not reach the main stem directly but discharges to oxbow lakes. Limited sampling of mines in this area has been conducted by Okanogan County and some arsenic elevations have been found (Raforth, 2000). For example, Ruby Mine had 196 ug/L arsenic in adit drainage and 4,512 mg/Kg arsenic in soil. Until recently, extensive tailings piles bordered the river at the Kabba-Texas Mine just above Nighthawk. However, arsenic levels in this material are low, 7 – 12 mg/Kg (Ecology and Environment, 1991; Johnson, 1997), and the piles were recently moved to an upland storage site.

There is much less runoff and little mining activity downstream of Nighthawk, where the potential sources appear limited to intermittent streams, orchard runoff, and the former Oroville municipal landfill. The landfill, which was the subject of a recent cleanup, is located on BLM land on the left bank, downstream of Enloe Dam. Arsenic is among the contaminants that have been identified at this site (Roy F. Weston, Inc., 1995). Fruit orchards are located along both sides of the lower river, beginning at about river mile 7.

Tentative sampling locations for the intensive surveys are shown in Figure 2. The following seven sites will be sampled on the main stem of the river:

- Chopaka bridge, B.C. (r.m. 36.1)
- Private road access (r.m. 23.8)
- Above Kabba-Texas Mine (r.m. 19.2)
- Nighthawk bridge (r.m. 17.5)
- Eagle Rock (r.m. 11.7)
- Enloe Dam (r.m. 8.9)
- Oroville bridge (r.m. 5.0)

The actual number of tributary and other source-related sites sampled will vary with runoff conditions encountered at the time of the surveys. As of this writing, all potential sources have not been identified. At a minimum, the following will be investigated for possible sampling (Figure 2):

- Jewett Creek
- Drainage below Golden Zone Mine
- Hurley Creek
- Anderson Creek

- Sheep Creek
- Drainage below Mountain Sheep Mine
- Drainage below Ruby Mine
- Drainage below Alice/Wyandotte Mines
- Palmer Creek (Palmer Lake Outlet)
- Lone Pine Creek
- Ellemham Draw Creek
- Old Oroville municipal landfill
- Orchard irrigation returns

Replicate samples will be collected at all main stem sites and analyzed for total recoverable and dissolved arsenic. The relative amounts of inorganic arsenic (+3, +5) and organic arsenic species will be determined on selected samples. Tributaries and other source-related samples will be analyzed for total recoverable arsenic, one sample from each per survey. Ancillary parameters will include conductivity, total suspended solids, hardness, flow, and temperature. Flow data for the main stem will be obtained from previously mentioned sources and from a USGS gage at Nighthawk.

Clean sampling techniques will be used for arsenic, following the guidance in EPA (1995) *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels.* The samples will be analyzed at the Ecology Manchester Environmental Laboratory by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The arsenic and hardness samples from routine monitoring will be held and analyzed with samples from the intensive surveys. There is a 6-month holding time for arsenic and hardness. Arsenic speciation will be done by Frontier GeoSciences.

Table 2 shows the tentative number and type of samples to be collected and an estimate of the laboratory costs. These estimates assume eight tributary or other source-related sites will be sampled during low flow, with 12 sites being sampled during high flow (20 total samples).

Table 2. Number of Samples and Laboratory Cost Estimate

Sample Type	Analysis	Stations or Samples	Sampling Events	Total Samples	Cost per Sample	Cost Subtotals
1. Routine Monitoring						
Main Stem Samples	Dissolved As	2	12	24	34	816
"	Total Recov. As	2	12	24	68	1632
2. Intensive Surveys						
Main Stem Samples	Dissolved As	14	2	28	34	952
"	Total Recov. As	14	2	28	68	1904
"	Hardness	7	2	14	12	168
"	TSS	7	2	14	10	140
"	Conductivity	7	2	14	7	98
"	As speciation	8	2	16	1440	2880
Source-Related Samples	Total Recov. As	10	2	20	68	1360
"	Hardness	10	2	20	12	240
"	TSS	10	2	20	10	200
"	Conductivity	10	2	20	7	140
Lab Duplicates (splits)	Dissolved As	2	2	4	34	136
"	Total Recov. As	2	2	4	68	272
Filter Blanks	Dissolved As	1	2	2	34	68
Bottle Blanks	Dissolved As	1	2	2	34	68
Matrix Spikes	Dissolved As	1	2	2	34	68
Matrix Spikes	Total Recov. As	1	2	2	68	136
Standard Ref. Material	As	2	2	4	no charge	0
Lab Control Sample	As	2	2	4	no charge	0
Method Blank	Dissolved As	2	2	4	no charge	0
Method Blank	Total Recov. As	2	2	4	no charge	0
					+0.45 micron filters @ $21 ea =	1218
					+500 mL Teflon bottles @ $14 ea =	1904
					+acid preservative @ $7 ea =	1344
					TOTAL LAB COST =	**$15,744**

Note: Cost of matrix spikes and SRM included in arsenic specation cost

Schedule

May 2000.....Routine monitoring begun
September 25-26, 2000...Low flow intensive survey
December 2000.....Laboratory analyses completed for May-October samples
May or June 2001.....High flow intensive survey
June 2001 .....Routine monitoring completed
August 2001..... ....Remaining laboratory analyses completed
October 2001.....Draft project report
December 2001.....Final project report
February 2002.....Data entered into EIM

Project Organization

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Ambient Monitoring - Kirk Smith (360/407-6680)
Supervisor – Rob Plotnikoff (360/407-6687)
Quality Assurance Officer – Cliff Kirchmer (360/407-6455)
Manchester Laboratory Director - Stuart Magoon (360/871-8801)
Manchester Inorganics Unit Leader- Jim Ross (360/871-8808)
Clients – Gary Passmore (509/634-2426) Mark Peterschmidt (509/454-7843)

Data Quality Objectives

Precision and Bias

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

Manchester's detection limit for arsenic by ICP-MS is 0.2 ug/L for both total recoverable and dissolved. Detection limits lower than the NTR arsenic criteria (0.14/0.018 ug/L) are not available through Manchester. Since concentrations in the river are an order of magnitude or more above 0.2 ug/L, this level constitutes the lowest concentration of interest and will meet the needs of the project.

Data quality objectives for arsenic speciation have not been set. Reporting limits are expected to be in the low ng/L range.

Sources of bias will be minimized by adherence to Method 1669 procedures for collection, preservation, transport, and storage of samples.

Representativeness

Large numbers of samples covering different seasons of the year are being collected in an effort to give results that are representative of arsenic concentrations in the Similkameen River. Because of the limited number of samples being collected from tributaries and other sources, these data may not be representative of arsenic concentrations during high flow conditions.

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 consistent with arsenic data EAP has previously obtained on the Similkameen and other Washington Rivers.

Sampling Procedures

Sampling methods for arsenic will follow the guidance in EPA Method 1669. Chain of custody will be maintained.

1. Routine Monitoring

Sampling methods for the routine arsenic monitoring done by FMU are similar to those that will be followed for the intensive surveys. FMU metals sampling methods are described in Hopkins (1996).

2. Intensive Surveys

Arsenic samples will be simple grabs collected by hand into pre-cleaned 0.5 liter Teflon bottles. These samples will be taken away from the bank by wading into the stream or using a pre-cleaned 0.5 liter Teflon bottle at the end of an aluminum pole. The dissolved samples will be filtered in the field through a pre-cleaned 0.45 um Nalgene filter unit (#450-0045, type S). For sites where both total recoverable and dissolved arsenic are being determined, half the contents of a Teflon bottle will be filtered, the remainder being the total recoverable sample for that site. The samples will

be acidified in the field to pH < 2 using 2-5mL of high-purity 1:1 nitric acid carried in Teflon vials. Teflon sample bottles, acid vials, and Nalgene filters will be obtained from Manchester, cleaned as described in Kammin et al. (1995), and sealed in plastic bags.

Non-talc nitrile gloves will be worn by personnel filtering the samples. Filtering will be done in a glove box constructed of a PVC frame and polyethylene cover. Each sample will be placed in double polyethylene bags and held on ice for transport to the laboratory.

Arsenic speciation samples will be simple grabs collected in 125 mL glass bottles with HCl as preservative, supplied by Frontier GeoSciences.

Samples for conductivity, hardness, and total suspended solids will be collected and preserved in polyethylene s bottles obtained from Manchester and held on ice for transport. The hardness bottles contain sulfuric acid as a preservative.

Flows will be measured with a Swoeffer or Marsh-McBirney meter and top-setting rod. Temperature will be determined with a precision mercury thermometer.

Analytical Procedures

Sample analysis will be conducted by Manchester Laboratory, except arsenic speciation by Frontier GeoSciences.

Arsenic will be analyzed by ICP-MS following EPA Method 200.8. Total recoverable arsenic samples will be digested with nitric acid following EPA Method 200.2, modified for ICP-MS. The target detection limit for arsenic will be 0.2 ug/L.

Arsenic speciation will be done by a modification of EPA Method 1632, employing hydride generation, cryogenic trapping, and ICP/MS.

Conductivity, hardness, and total suspended solids will be analyzed by Standard Methods 2510, EPA Method 130.2, and EPA Method 160.2, respectively

Quality Control Procedures

Field QC samples will include bottle blanks, filter blanks, and replicate samples.

The field blanks will be used to check for arsenic contamination arising from sample containers or the filtration procedure. Bottle blanks will consist of 0.5 liter Teflon bottles cleaned and filled with de-ionized (DI) water at Manchester Laboratory, as previously

described. Filter blanks will be prepared by filtering half the contents of a DI-filled Teflon bottle, the remainder being analyzed as the bottle blank. One field and one bottle blank will be prepared for each of the intensive surveys.

Field replicate samples and laboratory duplicate samples (splits) will be analyzed to provide an estimate of the variability affecting sample results due to sampling and analysis. All main stem samples for the intensive surveys are being collected in replicate. Replicates will consists of separate samples collected approximately five-ten minutes apart. Duplicate analyses will be conducted on one sample each from selected pairs of replicates. Two duplicates will be analyzed for each of the intensive surveys, one for the Chopaka bridge station and one for the Oroville station.

Manchester will analyze a freshwater standard reference material (SRM) for arsenic, SLRS-3 or equivalent. The arsenic concentration in SLRS-3 is certified at 0.72 +/- 0.05 ug/L. The SRM will be analyzed in duplicate for each sample set.

A laboratory control sample for arsenic (High Purity Standards, TMDW or equivalent) will be analyzed in duplicate with each sample set. The arsenic concentration in TMDW is 10 ug/L.

One matrix spike for total recoverable arsenic and one matrix spike for dissolved arsenic will be analyzed with each sample set. The spiking level should be within 1 – 10x the concentrations in the samples. A main stem sample will be selected for spiking and labeled as such.

Duplicate method blanks for arsenic will be analyzed with each sample set in order to determine the variability of the blank responses.

Laboratory QC samples for arsenic speciation will include a method blank, matrix spike, matrix spike duplicate, and an SRM. The SRM will be 1643d, certified for arsenic +5.

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 EPA 540/R-94-013, U.S. *EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, February 1994.*

The following additional information will be reported for Manchester's arsenic 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.

Frontier GeoSciences SOP for data reduction, review, and reporting will meet the needs of this project.

The project lead will prepare a draft report of the overall study by October 2001. 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 from results on QC samples, and the significance of any problems encountered in the analyses
- summary tables of the arsenic and ancillary data
- an evaluation of significant findings with respect to: extent and frequency of exceedances of NTR criteria; results of paired comparison tests for significant differences between upstream and downstream arsenic concentrations and loads; comparisons with Canadian data; arsenic source loadings and mass balance calculations; ranking of arsenic sources; and additional data interpretation as appropriate
- recommendations for follow-up work if warranted

A final report will be prepared after receiving review comments from the Colville Confederated Tribe, CRO, and EAP. The goal is to have the revised final report on or before December 2001.

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