

# An Environmental Investigation of the Quinsam Watershed

Prepared by

Environmental Sciences Group  
Royal Military College  
Kingston, Ontario

and

University of British Columbia

prepared for the

Canadian Water Network





## ACKNOWLEDGEMENTS

The environmental investigation of the Quinsam watershed was performed for and with the support of the Canadian Water Network/Réseau Canadien de l'Eau. The study was initiated in response to local concerns regarding the impact of the Quinsam Coal Mine on the Quinsam River watershed. The work was directed by Dr. William R. Cullen of the University of British Columbia (UBC).

The 2008/2009 field program to collect the sediments and mussels examined in this study was carried out by Dr. William R. Cullen and Vivian W.-M. Lai from UBC in the Quinsam watershed and mine site. They were assisted by Peter Winter, Barry Ross and Stan Goodrich from the Campbell River Environmental Committee (CREC) and personnel from the mine. Long-term monitoring of mussels was carried out by Dr. William R. Cullen and Vivian W.-M. Lai (UBC).

Laboratory analyses to determine levels of inorganic elements were carried out by ALS Environmental, in Vancouver, BC. The determination of arsenic in mussel tissues was carried out by Vivian W.-M. Lai at UBC. The determination of bioaccessible arsenic in selected sediments was carried out by John Peters, Sara Dillabough, Kim House and Tamara Van Dyck, and overseen by Dr. Iris Koch at the Environmental Sciences Group (ESG) research laboratories at the Royal Military College (Kingston, ON). X-ray absorption near edge structure (XANES) analyses were carried out by ESG personnel Maj. Louise Meunier, Dr. Mark Button and Maeve Moriarty at the Advanced Photon Source (APS), Argonne National Laboratories, Argonne, Illinois. Pacific Northwest Consortium X-ray Operations and Research (PNC/XOR) facilities at the APS, and research at these facilities, are supported by the US Department of Energy - Basic Energy Sciences, a Major Resources Support grant from NSERC, the University of Washington, Simon Fraser University and the Advanced Photon Source. Use of the Advanced Photon Source is also supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357. Assistance at APS was provided by Dr. Robert Gordon. Dr. Iris Koch and Maeve Moriarty conducted the data manipulations and statistical analyses.

This report was written by Vivian W.-M. Lai (UBC) and Dr. William R. Cullen (UBC), with assistance from Dr. Iris Koch (ESG) and Maeve Moriarty (ESG). Dr. Ken Reimer (ESG) provided editing assistance. The report was edited by Jane Bailey (ESG), graphic design was produced by Bill Duffe (ESG), and maps were produced by Alaina Leslie (ESG). Deborah Reimer (ESG) oversaw financial administration.



## **EXECUTIVE SUMMARY**

An environmental investigation of the Quinsam watershed, located on Vancouver Island, British Columbia was directed by Dr. William R. Cullen.

This study was initiated to investigate whether the mine was introducing arsenic into the watershed and if so, what the effects of arsenic input were on biota in the watershed. To determine natural and anthropogenic elemental loadings in sediments in the area, sediments were collected from a number of background lakes and lakes on the mine property, including the lake of highest concern, Long Lake. These results were compared with waste material from the mine site. The uptake of arsenic was investigated by using mussels in both short and long-term monitoring studies. A short-term caged mussel experiment was designed to investigate the potential for arsenic uptake, while long-term monitoring of mussels downriver of the mine was used to investigate current and historical arsenic loading in mussels.

Anthropogenic inputs of elements, including arsenic, to the watershed were identified after collected lake sediments were analyzed. In particular, Long Lake sediments were found to be elevated in arsenic. Further speciation analysis and bioaccessibility, or solubility, testing indicated that the introduced arsenic contamination can be easily solubilized and is more soluble than arsenic in the waste rock from the mine site. These speciation and bioaccessibility tests indicate that Long Lake sediments have forms and solubilities of arsenic similar to those from surrounding lakes. Further study is required to identify which of many potential sources around Long Lake is responsible for the elevated arsenic concentrations. The lake that flows into Long Lake, No Name Lake, was previously identified as also having elevated arsenic concentrations (Nordin, 2006) and the current study obtained similar results.

Elevated arsenic concentrations in sediments were found to correlate with elevated arsenic concentrations in biota. During the short-term caged mussels experiment higher arsenic loadings were found in mussels in Long Lake than in surrounding Quinsam watershed lakes. Higher loadings were seen in mussels collected from the Quinsam River in relation to the same species of mussel monitored in a nearby watershed, Simms Creek.

Arsenic concentrations are elevated in Long Lake as a result of acid rock drainage and other chemical process associated with mine waste. The high arsenic levels are associated with high concentrations of sulphate. The arsenic is available to bivalves, and presumably other biota. Further studies to identify the points of arsenic input should be undertaken to allow for corrective action. In particular sediment cores would provide evidence of the extent of anthropogenic arsenic inputs since the mine opening.



## TABLE OF CONTENTS

<b>Executive Summary .....</b>	<b>ii</b>
<b>I. Introduction.....</b>	<b>1</b>
<b>II. Background .....</b>	<b>4</b>
A. Site Location and History.....	4
B. Previous Studies .....	4
C. Experimental Approach.....	9
1. Project 1 .....	9
2. Project 2 .....	13
<b>III. Methods.....</b>	<b>15</b>
A. Principal Components Analysis (PCA).....	15
B. X-ray Absorption Near Edge Structure (XANES) Analysis .....	15
C. Physiologically Based Extraction Test (PBET) .....	16
D. Arsenic Analysis of Mussel Tissues .....	17
<b>IV. Results for Project 1.....</b>	<b>18</b>
A. PCA .....	18
B. Physiologically Based Extraction Test (PBET) .....	27
<b>V. Results for Project 2.....</b>	<b>30</b>
A. Caged Mussel Experiment .....	30
B. Long-term monitoring of the Quinsam watershed .....	32
<b>VI. Conclusion .....</b>	<b>33</b>
<b>VII. Use of Report .....</b>	<b>34</b>
<b>References .....</b>	<b>35</b>
<b>Appendix A: Data .....</b>	<b>A-i</b>
<b>Appendix B: QA/QC.....</b>	<b>VII-2</b>
<b>Appendix C: Acid Rock Drainage (ARD) and Arsenic Cycling.....</b>	<b>C-i</b>

## LIST OF FIGURES

Map I-1: Quinsam watershed overview. QM = main collection point for Lower Quinsam River black western pearl shell (*Margaritifera falcata*) mussels and SM = collection point for Simms Creek black western pearl shell mussels. ....2

Map I-2: Quinsam Coal mine site overview. CW = Coal washing plant, NTP = North tailings pond, STP = South tailings pond (where fine refuse is currently being stored), SP = settling ponds. High sulphur coal refuse is stored subaqueously in 3 South subaqueous storage. ....3

Map II-1: Quinsam sampling locations. Green = arsenic below 11 ppm, the interim BC sediment guideline for sensitive aquatic habitats; yellow = arsenic below 20 ppm, the interim BC guideline for typical sediments; and red = arsenic above 20 ppm and above all sediment BC and federal guidelines. LL = Long Lake, LLE and SPC = Long Lake settling pond and culvert, NNL = No Name Lake, ML = Middle Quinsam Lake, LQL = Lower Quinsam Lake, WL = Wokas Lake, and UQL = Upper Quinsam Lake. ....10

Map II-2: Long Lake sampling locations. Green = arsenic below 11 ppm, the interim BC sediment guideline for sensitive aquatic habitats; yellow = arsenic below 20 ppm, the interim BC guideline for typical sediments; and red = arsenic above 20 ppm and above all sediment BC and federal guidelines. LL = Long Lake, LLE and SPC = Long Lake settling pond and culvert, and NNL = No Name Lake. ....11

Map II-3: Map of locations for brown western floater mussels (*Anodonta kennerlyi*) cage locations for arsenic uptake study. ....14

Figure IV-1. Factor scores resulting from PCA of 41 elements for samples from different lakes in the Quinsam watershed. C = coarse mine tailing from 2 North pit, F = fine mine tailing, Coarse Refuse = from 3 South pit access road, SPC and LLE = Settling pond and culvert sediments, UQL = Upper Quinsam Lake, LQL = Lower Quinsam Lake, LLYP = Long Lake Yellow Point, NNL = No Name Lake, ML = Middle Quinsam Lake, LL = Long Lake. Refer to Maps II-1 and 2 for sample locations. Factor 1 explains 30 percent of the total variance in the data set, and Factor 2 explains 28 percent of the total variance. Red circle highlights grouping of Long Lake sediments LL2-LL6. Blue circle highlights grouping of remaining mine property lake sediments. ....23

**LIST OF FIGURES, CONT'D**

Figure IV-2. XANES results from Quinsam sediments. Three arsenic standards are shown along the bottom of this figure: arsenopyrite, solid arsenite (As(III)-O) and solid arsenate (As(V)-O). The lowest energy peak of the standards corresponds to the peak that would be observed if pyritic arsenic were present, and is not seen in any of the samples. The first peak, with the lowest energy, found in samples corresponds to an As(III)-O form of arsenic, and the second peak to an As(V)-O form. Solid lines indicate collected data, and dotted lines indicate fit. Blue scans indicate wet sediments.....25

Figure V-1. Arsenic concentration (ppm dry weight) in western floater mussels (*Anodonta kennerlyi*) over time. Data from all cages for each lake are combined. The error bars shown are the standard error from pooled samples from caged mussels from all cages from each lake. ....31

Figure V-2. Arsenic concentrations in black western pearl shell (*Margaritifera falcata*) mussels in the Lower Quinsam River and Simms Creek. The solid line shows the least squares fit of Simms Creek data over time. The dotted lines show the least squares fit of data both with and without the data point 1997 (circled in red). ....33

Figure A-1. Elemental loadings from the first two factors of the principal components analysis. Factor 1 explains 30 % of the total variance in the data set, and Factor 2 explains 28 % of the total variance. ....VII-1



## LIST OF TABLES

Table II-1. Previous Quinsam watershed sediment analytical results. Italicized results are above a BC guideline value for As, and above the CCME probable effect level for Fe and Mn. SS = sediment sample identifier used by Golder. ....6

Table II-2. Range of analytical results for runoff water measured by the Quinsam Coal Mine from test pads during the 2008/2009 reporting year (QCC, 2010). ....8

Table IV-1. Arsenic (As), iron (Fe) and manganese (Mn) concentrations in sediments from the Quinsam watershed. Italicized results are above a BC guideline value for As, and above the CCME probable effect level for Fe and Mn. Sample labels increasing in number indicate geographical locations that move from east to west in each specific lake. ....19

Table IV-2. Arsenic X-ray absorption near edge structure (XANES) results for wet and dried sediments from the Quinsam watershed. Wet samples are underlined. LL = Long Lake, LLE and SPC = sediments from settling pond and drainage at northeast end Long Lake, UQL = Upper Quinsam Lake.....24

Table IV-3. Arsenic bioaccessibility in selected sediments and coal refuse samples. ....28

## LIST OF PHOTOGRAPHS

Photograph II-1: 3 South pit access road, where coal refuse sample was collected, facing southwest.....13



## LIST OF ABBREVIATIONS

Abbreviation	Full Name
ABA	acid base accounting
AP	acid generating potential
ARD	acid rock drainage
As	arsenic
BC	British Columbia
CCME	Canadian Council of Ministers of the Environment
CREC	Campbell River Environment Committee
CWN/RCE	Canadian Water Network/ Réseau Canadien de l'Eau
ESG	Environmental Sciences Group (RMC)
Fe	iron
ICP-MS	inductively coupled plasma mass spectrometer
LL	Long Lake
LLE	Long Lake East
Mn	manganese
MQL	Middle Quinsam Lake
NNL	No Name Lake
NP	neutralization potential
NPR	net potential ratio
PAH	polycyclic aromatic hydrocarbon
PBET	physiologically based extraction test
PCA	principal components analysis
ppm	parts per million; equivalent to $\mu\text{g/g}$ (microgram of substance per gram of soil or sediment sample) and ppm (milligrams of substance per litre of aqueous solution)
ppb	parts per billion; equivalent to $\text{ng/g}$ (nanograms of substance per gram of soil or sediment sample) and $\mu\text{g/L}$ (micrograms of substance per litre of aqueous solution)
QCC	Quinsam Coal Corporation
RMC	Royal Military College
SPC	settling pond culvert
UBC	University of British Columbia
UQL	Upper Quinsam Lake
XANES	X-ray absorption near edge structure



## I. INTRODUCTION

A study released by the Province of British Columbia Ministry of Environment in 2006 attracted considerable public notice because the study reported elevated concentrations of some elements, including arsenic, in lake sediments near the Quinsam Coal Mine, near Campbell River, British Columbia (see Map I-1 for coal mine location), compared with BC provincial sediment guidelines of 11 ppm arsenic for sediments containing sensitive aquatic habitats and 20 ppm arsenic for typical sediments (Nordin, 2006). Members of the Canadian Water Network/Réseau Canadien de l'Eau (CWN/RCE) became aware of the public concern that elements were elevated and made presentations to the Campbell River Town Council and to Jim Mattison, assistant deputy minister of the Water Stewardship Division Ministry of Environment in June 2008. Following these meetings, Dr. William R. Cullen and members of the CWN/RCE undertook two projects, aided by the Environmental Sciences Group (ESG) of the Royal Military College, Kingston, ON. The mine made no direct financial contribution toward the projects but agreed to co-operate and mine staff provided valuable experience and resources.

There is general public concern over the health of the Quinsam watershed, in large part because of its importance as a fish habitat, especially for four species of salmon (chinook, coho, pink, and chum) and two species of trout (steelhead and cutthroat). The two projects included in this study investigate the effects of the mine on arsenic inputs to the watershed.

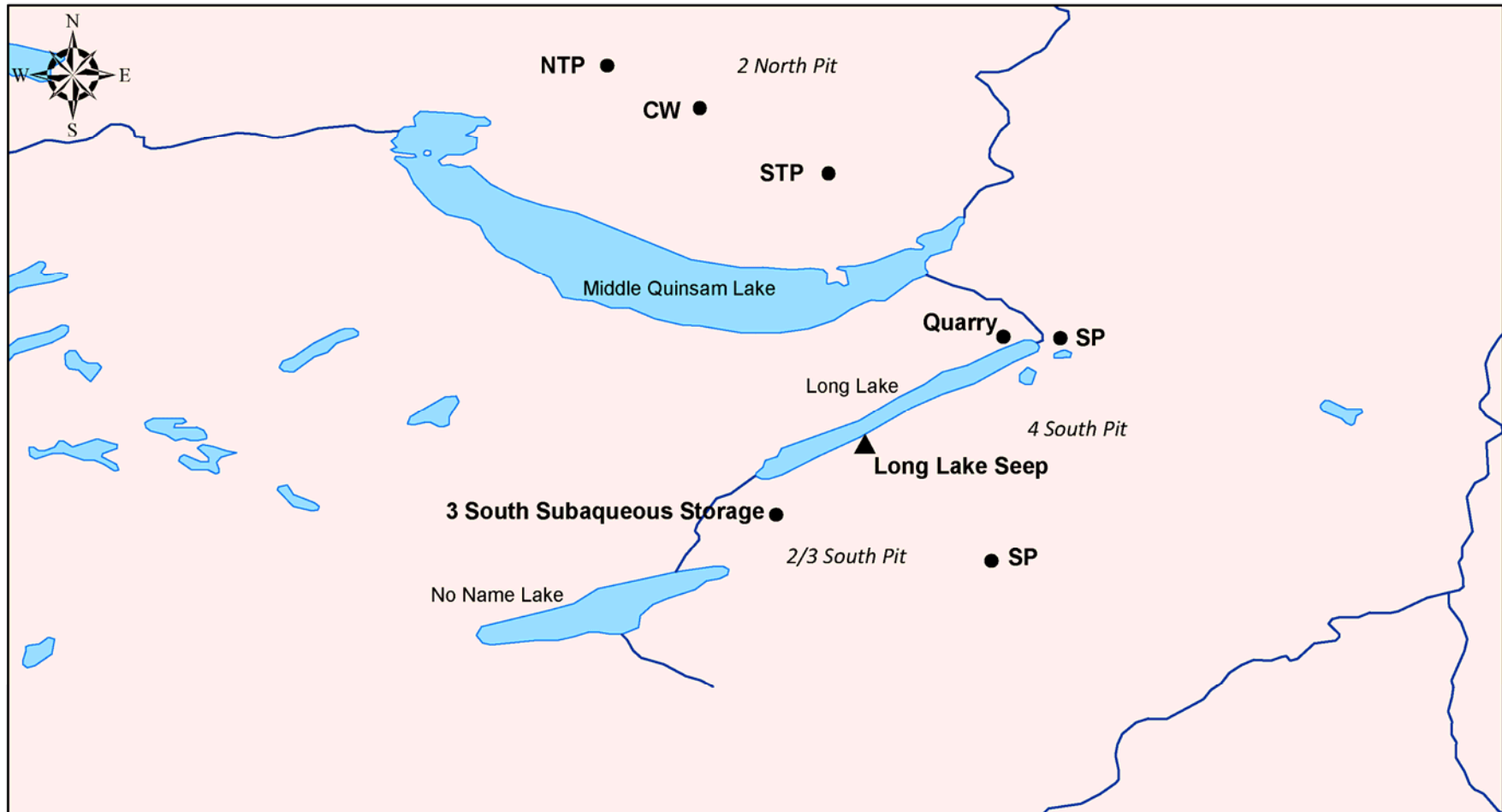
**Project 1.** To confirm that the arsenic concentrations in the sediments of Long Lake and No Name Lake are elevated and to establish the source of the arsenic.

**Project 2.** To probe the effects of the arsenic-rich sediments on biota by using fresh water mussels as an indicator species.

**Map I-1: Quinsam watershed overview. QM = main collection point for Lower Quinsam River black western pearl shell (*Margaritifera falcata*) mussels and SM = collection point for Simms Creek black western pearl shell mussels.**



**Map I-2: Quinsam Coal mine site overview.** CW = Coal washing plant, NTP = North tailings pond, STP = South tailings pond (where fine refuse is currently being stored), SP = settling ponds. High sulphur coal refuse is stored subaqueously in 3 South subaqueous storage.



## **II. BACKGROUND**

### **A. Site Location and History**

The Quinsam Coal Mine (Quinsam Coal Corporation (QCC), a division of Hillsborough Resources Limited) occupies 300 acres and is located approximately 30 km west of Campbell River, BC on Vancouver Island (see Map I-1). Open-pit mining began in 1986, and underground operations began in 1990. Open-pit and underground mining occurred adjacent to the south shore of Long Lake. All mining has been underground since 1994. Active underground mining is currently occurring north of Middle Quinsam Lake in 2 North pit, and coal wastes are stored near both Middle Quinsam Lake and Long Lake (see Map I-2) (QCC, 2010). No Name Lake flows into Long Lake.

Arsenic concentrations in Quinsam sandstone and mudstone are considerable, up to a maximum measured concentration of 410 ppm (QCC, 2010). Selected analytical data from the area of the proposed mine expansion is included in Table C-2 Appendix C. Arsenic can be incorporated up to 4.4 percent into the structure of pyrite,  $\text{FeS}_2$  (Cullen, 2008) and the Quinsam coal seams are layered between beds of siltstone and sandstone which often contain pyritic arsenic (QCC, 2010).

### **B. Previous Studies**

Three previous studies have reported arsenic concentrations in Quinsam watershed sediments, and results are summarized in Table II-1. A 1992 study of British Columbia lakes included a single sediment sample from Long Lake which had an arsenic concentration of 200 ppm, while two nearby lakes were sampled and were found to have lower arsenic concentrations (Rieberger, 1992). The Long Lake arsenic concentration is above both the BC arsenic sediment guideline, and the mean arsenic concentration of British Columbia lake sediments of  $45 \pm 150$  ppm (Rieberger, 1992).

A two-year (September 2003/2004) study performed by the BC Ministry of the Environment reported that arsenic, manganese, and iron concentrations in sediments from Long Lake and No Name Lake were elevated (Nordin, 2006). Elevated arsenic levels were not found in two nearby lake sediments, Upper Quinsam Lake and Middle Quinsam Lake (Nordin, 2006). Nordin (2006) concluded while contamination in the area was not widespread, the high arsenic concentrations found in sediments from Long Lake may be affecting the aquatic life. The Ministry of the Environment is responsible for ensuring the health of the Quinsam watershed.



A follow-up study by Golder Associates in 2007 (Golder, 2008) analyzed a limited number of sediment samples for arsenic from Long Lake and one sample from Upper Quinsam Lake. Moderately elevated arsenic sediment concentrations were reported in Long Lake sediments (23 to 58 ppm). A small number of toxicity studies were undertaken, including that of a freshwater amphipod (*Hyaella azteca*) in Long Lake sediments, but results were inconclusive (Golder, 2009).

None of these previous studies included a comprehensive and systematic sampling of lake sediments in the Quinsam watershed.

**Table II-1. Previous Quinsam watershed sediment analytical results. Italicized results are above a BC guideline value for As, and above the CCME probable effect level for Fe and Mn. SS = sediment sample identifier used by Golder.**

Report	Sample ID	Nearest Sample Collected in Current Report	As	Fe	Mn
			[ppm]	%	[ppm]
<i>BC Generic Contaminated Sediment Guideline (Sensitive)</i>			<i>11</i>	<i>n/a</i>	<i>n/a</i>
<i>BC Generic Contaminated Sediment Guideline (Typical*)</i>			<b>20</b>	<i>n/a</i>	<i>n/a</i>
<i>Interim Sediment Quality Guideline (ISQG), CCME</i>			5.9	2.1	460
<i>Probable Effect Level (PEL), CCME</i>			17	<b>4.4</b>	<b>1,100</b>
<b><i>Upper Quinsam Lake (UQL)</i></b>					
Golder, 2008	UQLSS#1	UQL4 & UQL5	<5.0	1.9	290
<b><i>Long Lake (LL)</i></b>					
Golder, 2008	LLSS#1	LL3	<b>51</b>	<b>6.9</b>	780
Golder, 2008	LLSS#2	LL3	<b>57</b>	1.8	440
Golder, 2008	LLSS#3	LL1	<b>26</b>	3.2	760
Golder, 2008	LLSS#4	LL1	<b>23</b>	2.8	<b>1,400</b>
Nordin, 2006	LL outlet	LL1	<i>16</i>	2.3	<b>1,300</b>
Nordin, 2006	LL outlet	LL1	<i>15</i>	2.3	<b>2,400</b>
Nordin, 2006	LL at settling pond	LL1	<b>220</b>	3.9	<b>2,400</b>
Nordin, 2006	LL at seep	LL6	6.2	1.6	240
Nordin, 2006	LL at seep	LL6	5.3	1.4	210
Rieberger, 1992	n/a**	n/a	<b>200</b>	0.1	<b>1,600</b>
<b><i>No Name Lake (NNL)</i></b>					
Nordin, 2006	NNL outlet	NNL1	<i>12</i>	<b>5.1</b>	520
Nordin, 2006	NNL inlet	NNL2	<b>35</b>	1.8	830
<b><i>Middle Quinsam Lake (ML)</i></b>					
Rieberger, 1992	n/a	n/a	<b>21</b>	0.03	410
<b><i>Lower Quinsam Lake (a.k.a. Quinsam Lake, LQL)</i></b>					
Rieberger, 1992	n/a	n/a	<b>52</b>	0.1	640

\* Typical indicates that sediment does not contain sensitive aquatic habitat and for which sensitive management objectives apply

\*\*n/a indicates that no sampling location was indicated other than the deepest part of the lake



Mining produces large amounts of unwanted waste rock, some of which is coal refuse. Coal refuse is generated after lighter coal is extracted from bulk mine rock. At Quinsam Coal this is achieved using a water cyclone system (QCC, 2010). Coal refuse is then separated by size into coarse and fine fractions. All fine refuse has been deposited in the south tailings pond (STP) since 1994; it was previously deposited in the north tailings pond (NTP, see Map I-2) (QCC, 2010). Coarse refuse is sometimes used for construction, or if it is considered by the mine to pose risk, is stored subaqueously. Before 1998, coarse refuse from the 4 South pit and 2 North pit was combined and placed near STP, located north of Middle Quinsam Lake (see Maps I-2). After Oct. 1, 1998, all 4 South coarse refuse was placed subaqueously in the 3 South pit, located south of Long Lake (see Map I-2) (QCC, 2010).

In 2003, at the suggestion of the Ministry of Energy and Mines, QCC began field testing how coal refuse reacts on exposure to air (QCC, 2010). Three lined test pads were built using coarse refuse. Coarse refuse from 4 South pit, 2 North pit and a mixture of 4 South/2 North pit refuse (1:1 blend) were placed in each of the test pads (see Map I-2 for pit locations). Runoff water has been collected and analyzed monthly since January 2005, although in 2008 there was enough runoff in only four of the 12 months to collect a sample for analysis. Coarse refuse from 2 North pit, located north of Middle Quinsam Lake, had relatively benign runoff, while 4 South pit coarse refuse, located south of Long Lake, contained high acid, high sulphur and low alkalinity runoff. Arsenic leaching is seen for both the combined refuse and 4 South refuse. Results are summarized in Table II-2. Note that the coarse refuse submitted for analysis in the current study originated from 2 North pit, while the 4 South pit was not mined during the 2008 season.

**Table II-2. Range of analytical results for runoff water measured by the Quinsam Coal Mine from test pads during the 2008/2009 reporting year (QCC, 2010).**

Analytes measured	Test Pads		
	4 South	2 North	1:1 4South:2North
pH	1.51 - 2.24	7.02-8.04	2.13 - 2.69
Acidity [ppm]	2,260 - 27,800	1.2 -33	689 - 16,200
Alkalinity [ppm]	< 2	23.8 - 72.7	< 2
Sulphate [ppm]	2,330 - 20,500	4.46 - 25.6	1,010 - 12,800
Arsenic [ppm]	1.09 - 25.1	0.001 max	0.032 - 9.78
Iron [ppm]	576 -7150	0.457 max	134 - 4450
Manganese [ppm]	1.65 - 14.7	0.009 max	2.86 - 44

QCC monitors the Long Lake seep water discharge, flowing into Long Lake from the south (see Maps I-2 and II-2). This water is thought to be influenced by groundwater in the 2/3 South pit areas and possibly by the water quality in the 3 South subaqueous storage pond (QCC, 2010). The 3 South pit is used to store high sulphur refuse underwater to minimize oxidation and the water contains high levels of sulphate (194 - 1022 ppm; average 817 ppm). The seep has high levels of total iron (1.57 – 5.01 ppm) and dissolved iron (< 0.030 – 4.01 ppm); seep concentrations were consistently above the permitted discharge level of 0.5 ppm dissolved iron (with the exception of August, 2008) in 2008/2009 (QCC, 2010). Long Lake seep is considered a significant contributor of sulphate to Long Lake where sulphate concentrations averaged 630 ppm in 2008/2009 (range 519 -740 ppm; similar to the previous year’s average of 643 ppm). Total arsenic concentrations in the seep water ranged from 0.005 to 0.012 ppm (QCC, 2010). These results suggest that there could be a constant, albeit low, source of arsenic to Long Lake as a consequence of pyritic oxidation and acid rock drainage (ARD). A summary of the process of ARD that leads to elevated sediment arsenic concentrations is given in Appendix C.

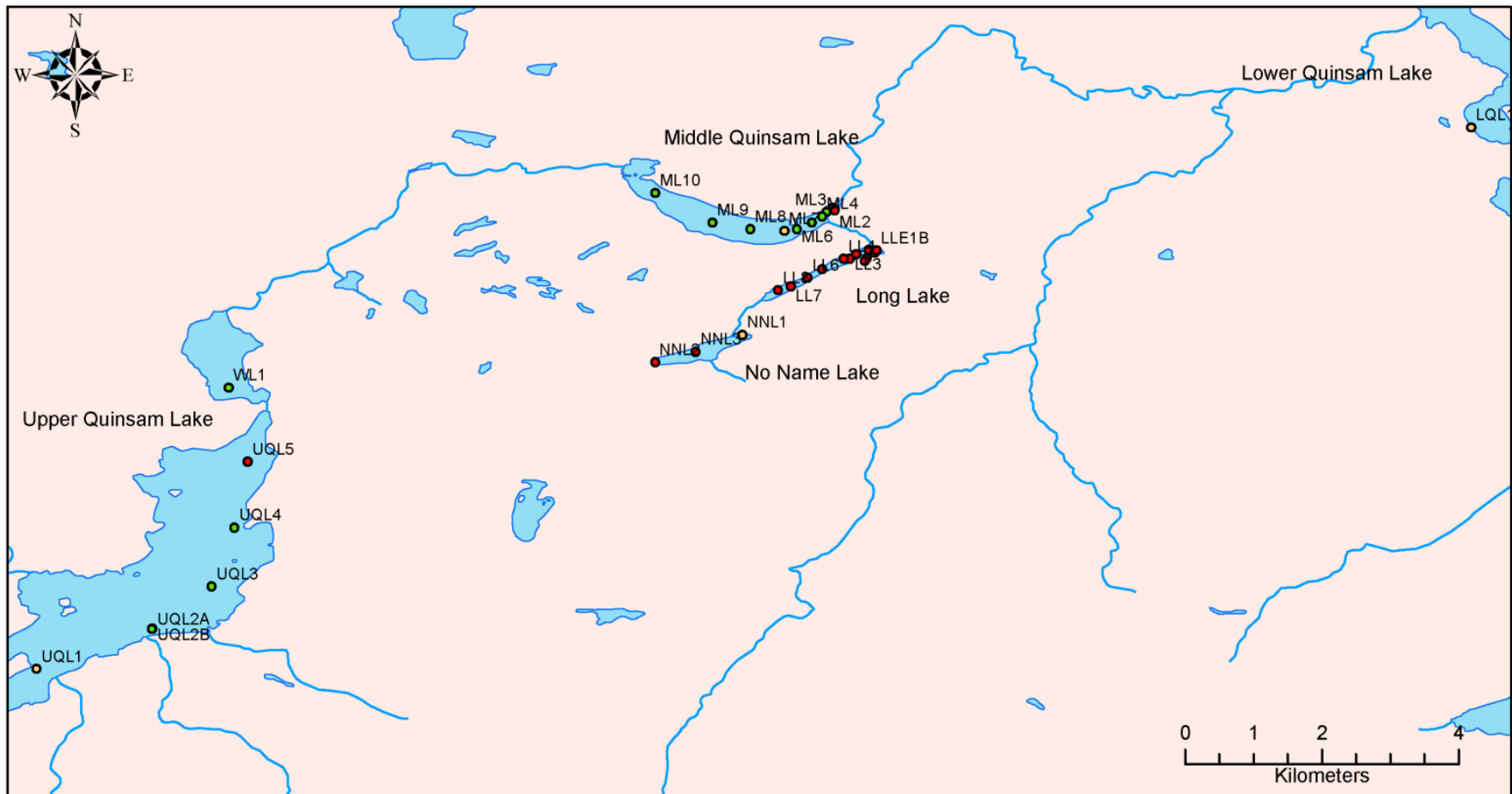
## **C. Experimental Approach**

### ***1. Project 1***

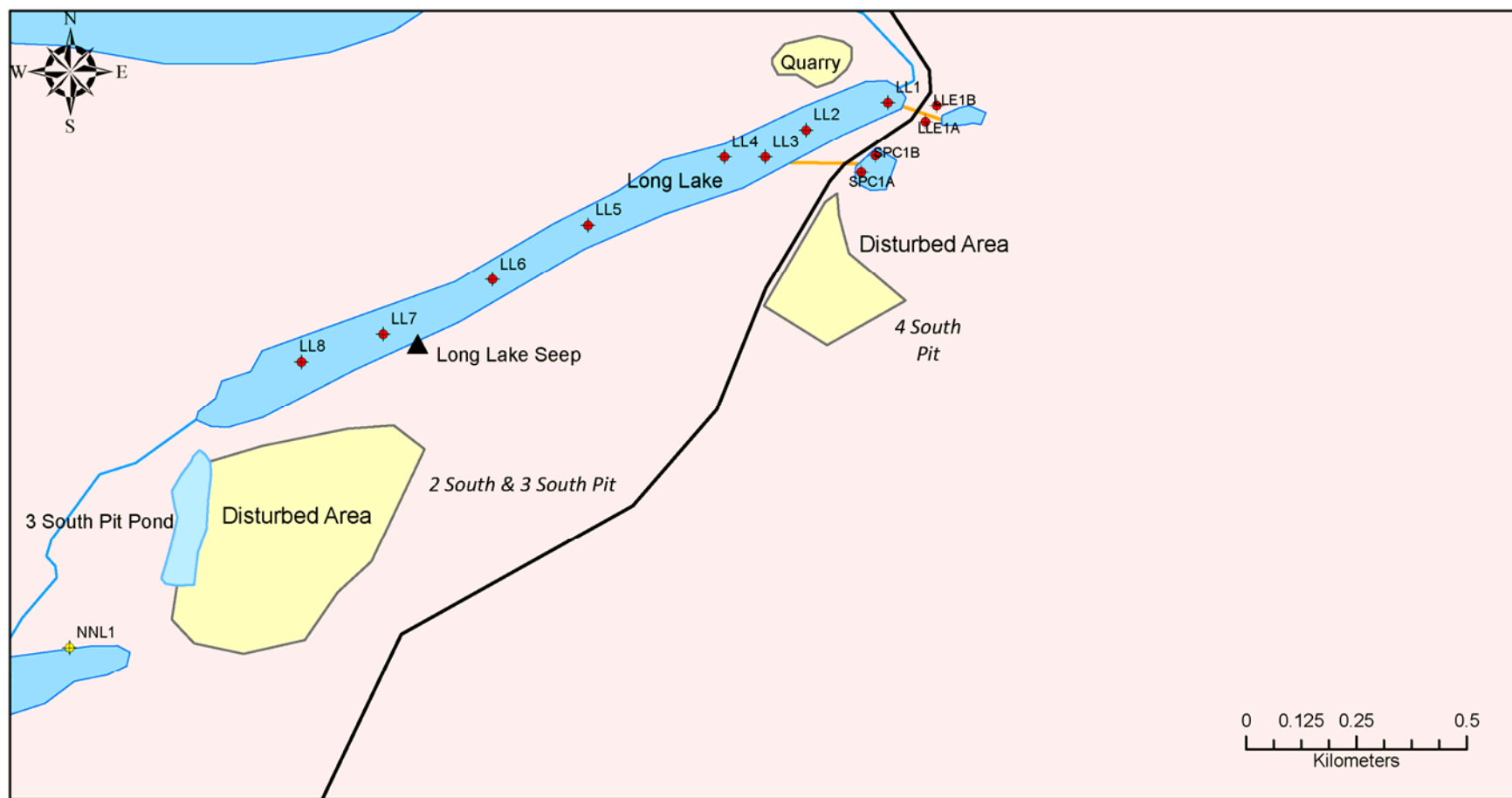
Sediment samples for the current study were collected in 2008 and 2009 from lake sites in a systematic manner. Samples were taken along the middle line of Middle Quinsam Lake, No Name Lake and Long Lake at regular intervals starting from one end and finishing at the other: the sites are shown in Maps II-1 and II-2. The same sampling plan was followed at Upper Quinsam Lake where possible: samples UQL2A, UQL2B, UQL3 and UQL4 were collected closer to the shore because of the depth of the lake. All sampling locations were independent of those chosen in previous studies. Two additional unimpacted lake sediment samples were collected from sites that were the source of mussels for Project 2, Lower Quinsam Lake, and a different Long Lake near Yellow Point (located south of Nanaimo). Where possible, two samples were collected at each site using an Ekman grab and were combined for analysis. The Ekman grab collects sediments from approximately 0-10 cm.

A number of mine waste samples were analyzed. One coal refuse sample was collected from the 3 South pit access road (Photograph II-1). Additional refuse samples were provided by the mine: three coarse and three fine refuse samples collected between 2007 and 2008. Coarse refuse (C1, C2, C3) originated from the 2 North pit (Map I-2), and the origin of fine samples was not specified.

**Map II-1: Quinsam sampling locations. Green = arsenic below 11 ppm, the interim BC sediment guideline for sensitive aquatic habitats; yellow = arsenic below 20 ppm, the interim BC guideline for typical sediments; and red = arsenic above 20 ppm and above all sediment BC and federal guidelines. LL = Long Lake, LLE and SPC = Long Lake petting pond and culvert, NNL = No Name Lake, ML = Middle Quinsam Lake, LQL = Lower Quinsam Lake, WL = Wokas Lake, and UQL = Upper Quinsam Lake**



**Map II-2: Long Lake sampling locations. Green = arsenic below 11 ppm, the interim BC sediment guideline for sensitive aquatic habitats; yellow = arsenic below 20 ppm, the interim BC guideline for typical sediments; and red = arsenic above 20 ppm and above all sediment BC and federal guidelines. LL = Long Lake, LLE and SPC = Long Lake pettling pond and culvert, and>NNL = No Name Lake.**



Three approaches were used in Project 1 to obtain multiple lines of evidence regarding the arsenic loading and its potential environmental mobility. The first approach employed a statistical multivariate analysis technique, principal components analysis (PCA), designed to obtain “fingerprints” of sediment samples based on their elemental composition. Since the combination of elements that give these fingerprints can be related to the source, the fingerprints can be used to distinguish between samples. This method has been used previously to distinguish between areas where arsenic concentrations are naturally elevated and where the arsenic is anthropogenic (Ollson, 2000; 2003).

The second approach made use of a spectroscopy technique to examine the chemical form, or speciation, of arsenic in a sample. The speciation of arsenic determines its environmental mobility and toxicity, and may be influenced by the source of arsenic. For soils and sediments, arsenic is almost entirely in inorganic forms which, when dissolved, can be toxic. Thus the key piece of information revealed by arsenic speciation for these samples is the solubility of arsenic. For example, in some mineralogical forms where arsenic-sulphur binding is prevalent (*e.g.* arsenopyrite,  $\text{FeAs}^{(1-)}\text{S}$ ) the arsenic is likely to be environmentally unavailable under most conditions. In contrast, in the trivalent oxidation state bound to oxygen (*e.g.* as  $\text{As}^{(3+)}_2\text{O}_3$ ) arsenic is more soluble.

Arsenic speciation was examined for the collected sediment samples by using X-ray absorption spectroscopy (XAS), specifically X-ray absorption near edge structure (XANES) spectroscopy. XANES has proved to be an accurate method to characterize arsenic in unprocessed solid samples, revealing speciation information that was consistent with bioaccessibility and PCA results (Ollson *et al.*, 2001, Koch *et al.*, 2007).

The third approach was the use of a physiologically based extraction test (PBET). This is a laboratory extraction that mimics the human gastrointestinal system. The PBET reveals the arsenic solubility of a sample in this environment, which is also referred to as the bioaccessibility of arsenic. The bioaccessibility information helps to corroborate the speciation information and offers another way to distinguish between sediments with different arsenic sources. Bioaccessibility has frequently been shown to be a good representation of bioavailability (*i.e.* the absorption of arsenic into the bloodstream) (Ruby *et al.*, 1996, Rodriguez *et al.*, 1999), and can be used to estimate the relative risk posed by the sediments to animals and humans, should exposure occur.

The above approach, consisting of using PCA, PBET, and XANES, was applied to determine if the elevated arsenic levels at Long Lake were a consequence of naturally elevated background arsenic chemistry, or a result of mine activity. The PCA technique was used to investigate any relationships between the analytical data and the sample location at No Name Lake.



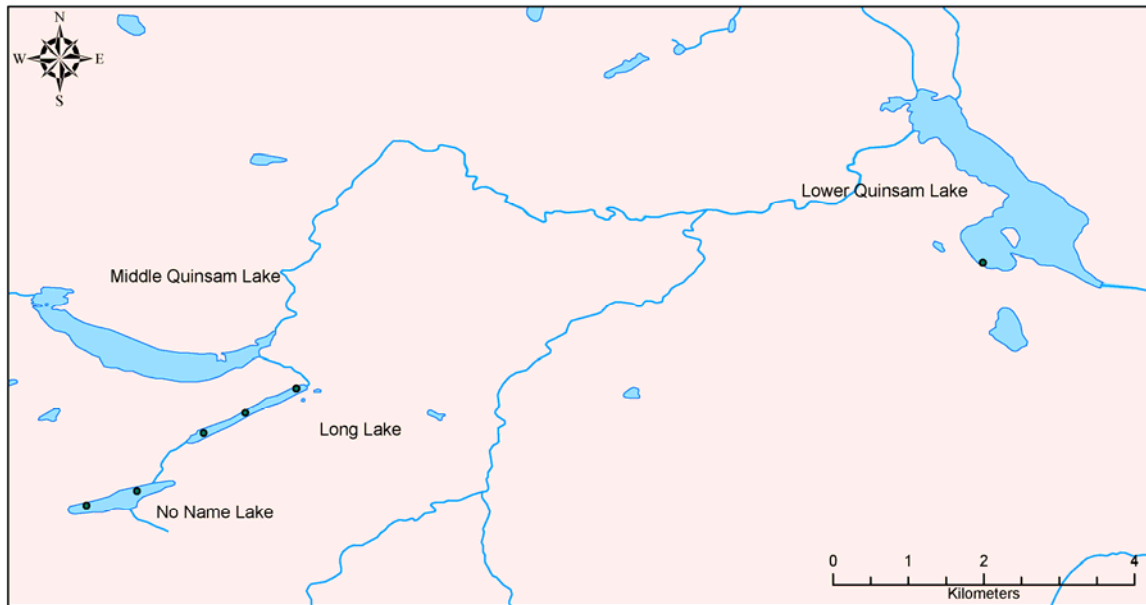
**Photograph II-1: 3 South pit access road, where coal refuse sample was collected, facing southwest.**

## ***2. Project 2***

In Project 2 the actual arsenic uptake by mussels in the watershed, both on the mine site, and a distance downriver, was investigated over time.

Seventy-two brown western floater mussels (*Anodonta kennerlyi*) were collected from the boat launch area of Lower Quinsam Lake on April 28, 2009. These were divided into six groups of 12 and placed in extruded polyethylene (Rurethene<sup>®</sup>) metal-free cages designed and constructed by the UBC chemistry department mechanical shop. One cage with its complement of mussels was retained at the launch site to act as a control, and the remaining five cages were placed in three sites in Middle Quinsam Lake (two near the inlet and outlet, and one in the centre of the lake) and two sites in Long Lake (near the inlet and outlet) (see Map II-3).

**Map II-3: Map of locations for brown western floater mussels (*Anodonta kennerlyi*) cage locations for arsenic uptake study.**



Samples from each site were collected six weeks, four months and six months later except from the control site where the cage was vandalized sometime before the six-week sampling event. Uncaged mussels were collected from this site as needed to act as control. Visual examination of previously caged mussels on collection did not indicate that they had been stressed.

Long-term monitoring of arsenic uptake into mussels by UBC began in 1997 (Koch *et al.*, 2001). The dominant mussel species found in the rivers in the Quinsam area is the black western pearl shell (*Margaritifera falcata*). Mussels from the Quinsam River were sampled downriver of the Quinsam River Hatchery, 5 km northwest of Campbell River (see QM on Map-I). In May and June, 2008, mussels were collected from one additional location upriver of the Quinsam River Hatchery (see Map I-1). Simms Creek is located south of Campbell River, east of the Quinsam watershed, and was used as the control site for these mussel experiments (see SM on Map I-1).

### III. METHODS

#### A. Principal Components Analysis (PCA)

PCA allows for multivariate pattern recognition of the concentrations of inorganic elements in samples by examining their position on a reduced (usually two or three dimensional) plot. The axes of the plot are linear combinations of the original  $n$  variables.

The variables in this statistical analysis were selected from concentrations of 51 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, and Zr. Numbers greater than zero are required for the statistical analysis and therefore any non-detectable values were replaced with half the detection limit. Three of these elements – gold (Au), boron (B) and tantalum (Ta) – were not included as more than 50 percent of the samples analyzed were below their detection limits.

Statistical analysis was carried out using Systat 12 software. The distribution of concentrations of each of the 48 variables (elements) in the 41-sample data set was examined and distribution for each variable were skewed (skewness ranged from -0.133 to 6.268).  $\log_{10}$  transformation reduced skewness (-1.489 to 1.664) to obtain more normal data distributions.  $\log_{10}$  transformed data were subsequently used in the PCA as this analysis assumes normal data distributions.

#### B. X-ray Absorption Near Edge Structure (XANES) Analysis

X-ray analysis was performed at the Pacific Northwest Consortium X-ray Operations and Research (PNC/XOR) facility on the bending magnet (BM) beamline at sector 20 of the Advanced Photon Source in Argonne, Illinois in December, 2008 and November, 2009. The Si(111) double-crystal monochromator for the BM line was calibrated using the first inflection point of the gold  $L_{III}$  absorption edge (11919.7 eV). The beam was detuned to 85 percent of maximum intensity and a rhodium-coated harmonic mirror was used to maximize harmonic rejection. Fluorescence data were collected using a solid-state Ge(Li) detector (Canberra model GL0055PS). Dried samples were prepared as four layers of powder on Kapton tape at the APS after grinding dried sediment samples in a ball mill. These were analyzed at room temperature. Wet samples were packed into sample holders between two layers of Kapton tape, and analyzed at 50 °K. For each sample, five scans were collected and averaged before background removal

and normalization to the edge jump. Examination of the X-ray absorption near-edge structure (XANES) spectra from first to last in each set showed no beam damage to the samples.

XANES spectra of the arsenic K-edge (11868 eV) were fit within -20 to +30 eV from arsenic's ionization energy,  $E_0$ , using ATHENA software (Ravel *et al.*, 2005). A reference gold foil was measured simultaneously with samples. Data were compared with linear combinations of reference compounds previously shown to distinguish between seven different groups of arsenic compounds based on the position of the main peak feature (Smith *et al.*, 2005). Inorganic arsenite ( $\text{As}^{3+}$ ,  $\text{As}_2\text{O}_3$ ) and arsenate ( $\text{As}^{5+}$ ,  $\text{KH}_2\text{AsO}_4$ ) standards were used (liquid for wet samples and solid for dried solids). Arsenopyrite was not included in any final fits because of its poor fit. All fits were constrained to sum to 100 % of measured arsenic. The two peaks correspond to As(III)-O (11871.7 eV) and As(V)-O (11875.3 eV).

### **C. Physiologically Based Extraction Test (PBET)**

The bioaccessibility of metals in soils and sediments can be estimated using extractions that simulate human gastrointestinal processes, also referred to as bioaccessibility tests. Bioaccessibility is the fraction of the total arsenic in soil (or sediment) that is solubilized during such extraction tests. Ruby *et al.*, (1996) published the first study examining the utility of a PBET. The extraction test takes into consideration gastric and intestinal pH, soil mass and fluid volume, stomach mixing, stomach emptying rate, small intestinal transit time, and gastrointestinal chemistry.

The method used in this report was adapted from Ruby *et al.*, (1996) and Rodriguez *et al.*, (1999). Each dried sample was ground with a mortar and pestle. To simulate stomach conditions, pepsin (1.25 g/L), sodium citrate (0.5 g/L), malic acid (0.5 g/L), glacial acetic acid (1 mL/L), and sodium chloride (8.8 g/L) were used to make the extraction solution, adjusted to pH 1.8 using hydrochloric acid and maintained at body temperature (37 °C). A liquid:solid ratio of 100:1 was used (dry weight): 0.2g of each sample was weighed into two 50-mL centrifuge tubes, and 20 mL of extraction solution was added, labelled phase one (P1) and phase two (P2). All samples were placed in an incubator set to 37 °C and shaken at 275 rpm (Innova 4230, New Brunswick Scientific). The pH was checked at 30 minutes and one hour. After one hour, P1 samples were removed and weighed, representing a gastric digestion. P2 samples were adjusted to pH 7 using a saturated sodium carbonate solution, then bile extract (1.875 mg/mL) and

pancreatin (0.5 mg/mL) were added. P2 samples were shaken for another four hours adjusting the pH when necessary. P2 samples were then removed and weighed representing gastric followed by intestinal digestion. All samples were centrifuged at 3800 rpm (3100  $\times$ g) for ten minutes and then filtered (0.45  $\mu$ m Millipore Millex-HV Hydrophilic PVDF filter) prior to performing dilutions and analysis.

Arsenic analyses were carried out using an X7 X-Series II, inductively coupled plasma mass spectrometer (ICP-MS) (Thermo Electron) using collision cell mode. The detection limit (1 ppb) was based on the lowest concentration arsenic standard used in the calibration curve. Arsenic ( $m/z$  75) was quantified using scandium, yttrium, indium, terbium, holmium and bismuth as internal standards to correct for instrument drift and matrix effects. Mass interferences from chloride were monitored as  $m/z$  77( $\text{ArCl}^+$ ) and automatically corrected by the PLASMALAB<sup>TM</sup> software.

#### **D. Arsenic Analysis of Mussel Tissues**

Mussel tissues were frozen in dry ice upon collection and transferred to a freezer at  $-20^{\circ}\text{C}$  until dissection if required. Otherwise, the flesh from three to five mussels at each site was combined and freeze dried. Dry samples were ground using mortar and pestle.

Mussel samples ( $\sim 0.1$  g) were weighed into glass test tubes. To each tube was added 2 mL of nitric acid and 3 Teflon<sup>®</sup> boiling chips. The samples were kept at room temperature overnight and on the second day heated in a test tube block heater at temperatures increasing stepwise from 50 to 120  $^{\circ}\text{C}$  and then cooled overnight. Hydrogen peroxide (2 mL) was added into the samples on the third day, and the samples were heated to 150  $^{\circ}\text{C}$  until they were evaporated to dryness. The residue was redissolved in 3 mL of an aqueous solution containing 1% (v/v) nitric acid and 5 ppb rhodium. Samples were mixed thoroughly by using a vortex mixer and filtered (0.45  $\mu$ m). Samples were stored at 4 $^{\circ}\text{C}$  until analysis.

Samples after digestion were diluted as needed with the rhodium-nitric acid solution and analyzed using ICP-MS. A double-focusing magnetic sector field ICP-MS (Element2, Thermo Finnigan, Germany) equipped with a Conikal nebulizer was used as a detector. The instrument was operated at low-resolution mode ( $R = 300$ ). The mass analyzer was set to monitor both the  $m/z = 75$  signal peak corresponding to  $\text{As}^+$  and the  $m/z = 77$  corresponding to the interference possibly caused by the chloride in the samples ( $\text{ArCl}^+$ ). Since  $m/z = 77$  also corresponds to  $^{77}\text{Se}^+$ ,  $^{82}\text{Se}^+$  was also monitored to correct for



the Se portion of the counts collected under  $m/z = 77$  signal peaks. Signals from replicated runs were averaged to give the counts. Signals were corrected according to the signal of the internal rhodium standard. Data were collected and were manipulated on a separate computer (MS Excel).

## **IV. RESULTS FOR PROJECT 1**

### **A. PCA**

The two previous studies by Nordin (2006) and Golder (2008) indicated that elevated arsenic concentrations were present in Long Lake. Only one sample from the upriver unimpacted Upper Quinsam Lake was sampled and observed to have an arsenic concentration below the British Columbia interim sediment guideline (see Table II-1) (Golder, 2008). The current study includes a larger number of sediments from the unimpacted lake, which allows for comparison with impacted lake sediments. Results for arsenic, iron and manganese concentrations are provided in Table IV-1. Results for all analytes are provided in Table A-1, Appendix A.

**Table IV-1. Arsenic (As), iron (Fe) and manganese (Mn) concentrations in sediments from the Quinsam watershed. Italicized results are above a BC guideline value for As, and above the CCME probable effect level for Fe and Mn. Sample labels increasing in number indicate geographical locations that move from east to west in each specific lake.**

Sample ID	As	Fe	Mn
	[ppm]	%	[ppm]
Analytical Limits of Reporting	0.1	0.01	5
<i>BC Generic Contaminated Sediment Guideline (Sensitive aquatic habitat)</i>	<i>11</i>	<i>n/a</i>	<i>n/a</i>
<i>BC Generic Contaminated Sediment Guideline (Typical)</i>	<i>20</i>	<i>n/a</i>	<i>n/a</i>
<i>Interim Sediment Quality Guideline (ISQG)</i>	<i>5.9</i>	<i>2.1</i>	<i>460</i>
<i>Probable Effect Level (PEL)</i>	<i>17</i>	<i>4.4</i>	<i>1,100</i>
<b><i>Long Lake (East to West) (LL)</i></b>			
LL1	<i>36</i>	<i>3.1</i>	<i>1,900</i>
LL2	<i>630</i>	<i>13</i>	<i>22,000</i>
LL3	<i>140</i>	<i>9.1</i>	<i>4,000</i>
LL4	<i>110</i>	<i>8.6</i>	<i>2,000</i>
LL5	<i>240</i>	<i>14</i>	<i>3,300</i>
LL6	<i>360</i>	<i>11</i>	<i>28,000</i>
LL7	<i>26</i>	<i>3.7</i>	<i>600</i>
LL8	<i>30</i>	<i>3.0</i>	<i>1,500</i>
<b><i>Middle Quinsam Lake (East to West) (ML)</i></b>			
ML1	<i>9.9</i>	<i>2.1</i>	<i>1,700</i>
ML2	<i>34</i>	<i>4.0</i>	<i>620</i>
ML3	<i>8.1</i>	<i>1.7</i>	<i>330</i>
ML4	<i>6.5</i>	<i>1.3</i>	<i>340</i>
ML5	<i>6.7</i>	<i>1.5</i>	<i>260</i>
ML6	<i>8.5</i>	<i>2.6</i>	<i>420</i>
ML7	<i>12</i>	<i>3.3</i>	<i>740</i>
ML8	<i>6.5</i>	<i>1.9</i>	<i>300</i>
ML9	<i>9.2</i>	<i>3.4</i>	<i>710</i>
ML10	<i>6.8</i>	<i>2.4</i>	<i>510</i>

**Table IV-1 cont'd. Arsenic (As), iron (Fe) and manganese (Mn) concentrations in sediments from the Quinsam watershed. Italicized results are above a BC guideline value for As, and above the CCME probable effect level for Fe and Mn. Sample labels increasing in number indicate geographical locations that move from east to west in each specific lake.**

Sample ID	As	Fe	Mn
	[ppm]	%	[ppm]
Analytical Limits of Reporting	0.1	0.01	5
<i>BC Generic Contaminated Sediment Guideline (Sensitive aquatic habitat)</i>	<i>11</i>	<i>n/a</i>	<i>n/a</i>
<i>BC Generic Contaminated Sediment Guideline (Typical)</i>	<i>20</i>	<i>n/a</i>	<i>n/a</i>
<i>Interim Sediment Quality Guideline (ISQG)</i>	<i>5.9</i>	<i>2.1</i>	<i>460</i>
<i>Probable Effect Level (PEL)</i>	<i>17</i>	<i>4.4</i>	<i>1,100</i>
<b><i>No Name Lake (East to West) (NNL)</i></b>			
NNL1	<i>13</i>	1.2	320
NNL3	<i>55</i>	<i>8.0</i>	930
NNL2	<i>50</i>	3.9	310
<b><i>Upper Quinsam Lake (South to North) (UQL)</i></b>			
UQL1	<i>13</i>	<i>5.6</i>	<i>1,800</i>
UQL2A	4.3	<i>5.7</i>	<i>710</i>
UQL2B	3.9	<i>5.6</i>	<i>640</i>
UQL3	4.5	3.2	<i>540</i>
UQL4	4.7	2.3	400
UQL5	<i>45</i>	<i>7.7</i>	<i>39,000</i>
<b><i>Wokas Lake (WL), Lower Quinsam Lake (LQL) and Yellow Point (LLYP)</i></b>			
WL1	9.1	3.6	890
LQL1	<i>13</i>	1.5	200
LLYP1	0.80	0.69	100
<b><i>Mine Site settling pond and drainage (LLE and SPC)</i></b>			
SPC1A	<i>21</i>	<i>4.8</i>	<i>710</i>
SPC1B	<i>22</i>	<i>5.0</i>	<i>740</i>
LLE1A	<i>22</i>	<i>4.9</i>	<i>470</i>
LLE1B	<i>24</i>	<i>4.8</i>	<i>540</i>

**Table IV-1 cont'd. Arsenic (As), iron (Fe) and manganese (Mn) concentrations in sediments from the Quinsam watershed. Italicized results are above a BC guideline value for As, and above the CCME probable effect level for Fe and Mn. Sample labels increasing in number indicate geographical locations that move from east to west in each specific lake.**

Sample ID	As	Fe	Mn
	[ppm]	%	[ppm]
Analytical Limits of Reporting	0.1	0.01	5
<i>BC Generic Contaminated Sediment Guideline (Sensitive aquatic habitat)</i>	<i>11</i>	<i>n/a</i>	<i>n/a</i>
<i>BC Generic Contaminated Sediment Guideline (Typical)</i>	<i>20</i>	<i>n/a</i>	<i>n/a</i>
<i>Interim Sediment Quality Guideline (ISQG)</i>	<i>5.9</i>	<i>2.1</i>	<i>460</i>
<i>Probable Effect Level (PEL)</i>	<i>17</i>	<i>4.4</i>	<i>1,100</i>
<b>Coal Refuse</b>			
Coal refuse (3 South pit)	<b>21</b>	<b>4.7</b>	460
C1	4.8	3.9	560
C2	10	3.5	500
C3	6.9	2.5	350
F1	6.5	3.7	580
F2	7.0	<b>7.4</b>	<b>1,600</b>
F3	7.6	2.7	340

An analysis of variance (ANOVA) indicates that sediment arsenic concentrations are significantly different between sediments and refuse in the studied lakes (ANOVA,  $N=8$ ,  $p < 0.001$ ). Pairwise comparisons using a Tukey's test ( $p < 0.05$ ) indicate that Long Lake sediment arsenic concentrations are significantly higher than those in sediments from Upper Quinsam Lake, Middle Quinsam Lake, Yellow Point, the mine settling pond and drainage ditch, and in coal refuse. No significant differences were seen between any lake sediments and No Name Lake, with the exception of No Name Lake being significantly higher than sediments from Yellow Point ( $p = 0.007$ ) which is located in a different watershed.

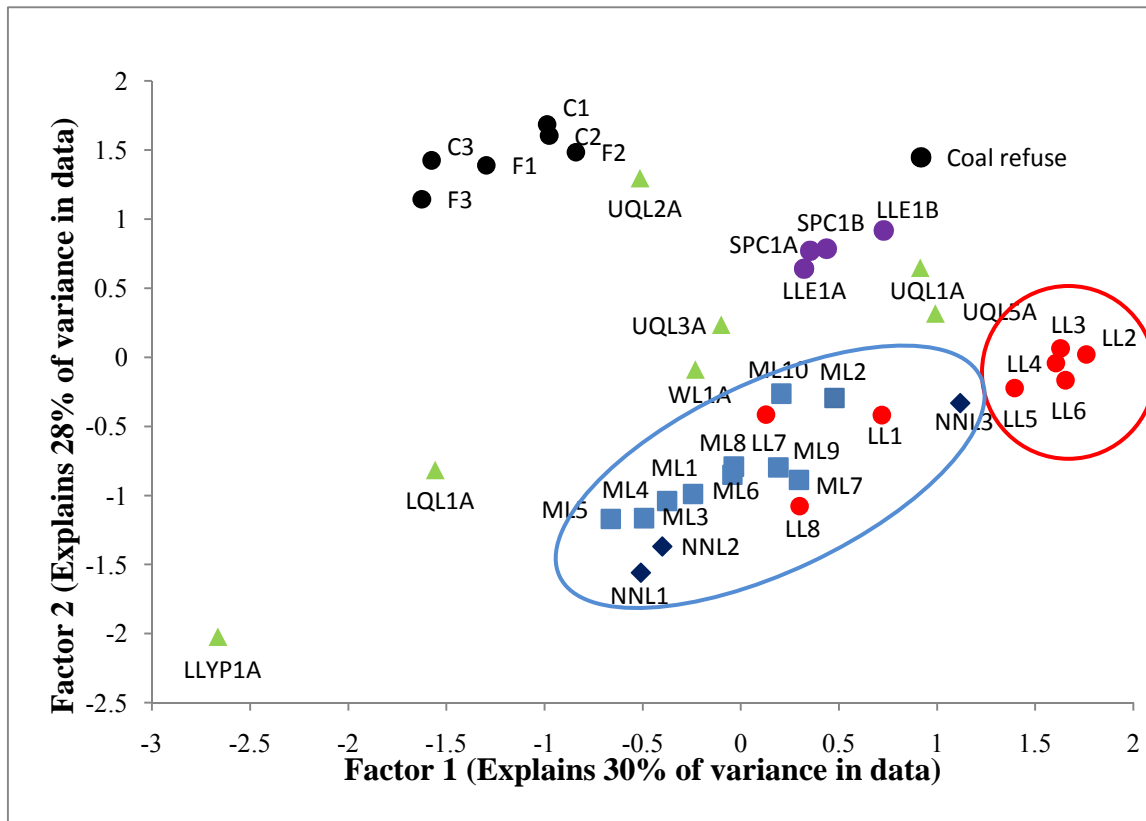
A PCA more effectively shows how these sediments are related overall. The PCA resulted in seven eigenvalues having a value greater than one. Together these seven new variables, or factors, explain 90 percent of the variation in the data, instead of the original

48 elements (variables). The first two factors explain 58 percent of the variance in the data (30 and 28 percent for factors one and two, respectively) from lake sediments. The principal component values for the first two factors for each sample are plotted below, and show how the samples are grouped (Figure IV-1). The component scores for the first two factors for all elements are plotted in Appendix A (Figure A-1). The contribution of all elements to the seven factors, as well as the percentage of variance they explain, is included in Table A-2 in Appendix A. Long Lake sediments, particularly LL2 – LL6, are grouped together on the positive side of Factor 1 and they are separate from the other samples, because of high element concentrations, including arsenic, iron and manganese. The PCA confirms these Long Lake samples are different from sediments collected from unimpacted lakes and from settling pond and drainage sediments. Differences between Long Lake sediments and those from unimpacted lakes suggest that the Long Lake sediments do not have similar elemental profiles to other lakes in the region.

Potential sources of arsenic to Long Lake identified by QCC include surface runoff impacted by the 2 South, 3 South and 4 South areas, the Long Lake seep, and seepage from the tailings settling ponds (QCC, 2010). Water from Long Lake seep reaches Long Lake southwest of LL6 and includes groundwater flow from the vicinity of the 2 South pit and 3 South pit which stores high sulphur coal wastes. The settling pond where sediments (SPC and LLE) were collected flow into the location of LL2 and LL3, areas with very high arsenic loadings as well.

Lake sediments were compared with coal refuse samples. One coal refuse sample was collected from the access road to 3 South pit. The remaining coarse and fine refuse samples (C1-3 and F1-3) were provided by the mine. Coarse refuse originated from the 2 North pit and the annual report indicates much of this material is used to raise the south tailings pond walls, north of Middle Quinsam Lake (Map I-2). Fine refuse was pumped from the Coal Wash Plant, located north of Middle Quinsam Lake, into the south tailings pond (QCC, 2010). The coal refuse sample collected from the 3 South tailings pond access road, the sediment samples collected from the north end lake setting ponds (SPC and LLE) and culverts, and the mine refuse provided by the mine (C1-3, F1-3) differed in elemental composition from all of the lake sediments. The lack of resemblance between Long Lake sediments and samples that represent potential sources indicates that the cause of contamination in Long Lake is likely not bulk mass transfer from the mine site, such as dumping or washing material from the surface or underground. The seep water data show a potential link between the 3 South pond and the elevated arsenic concentrations in Long Lake sediments. The arsenic concentrations measured in No Name Lake sediments during the current study are similar those previously reported by Nordin (2006). However, the PCA did not indicate significant anthropogenic impact.

**Figure IV-1. Factor scores resulting from PCA of 41 elements for samples from different lakes in the Quinsam watershed. C = coarse mine tailing from 2 North pit, F = fine mine tailing, Coarse Refuse = from 3 South pit access road, SPC and LLE = Settling pond and culvert sediments, UQL = Upper Quinsam Lake, LQL = Lower Quinsam Lake, LLYP = Long Lake Yellow Point, NNL = No Name Lake, ML = Middle Quinsam Lake, LL = Long Lake. Refer to Maps II-1 and 2 for sample locations. Factor 1 explains 30 percent of the total variance in the data set, and Factor 2 explains 28 percent of the total variance. Red circle highlights grouping of Long Lake sediments LL2-LL6. Blue circle highlights grouping of remaining mine property lake sediments.**



### XANES analysis

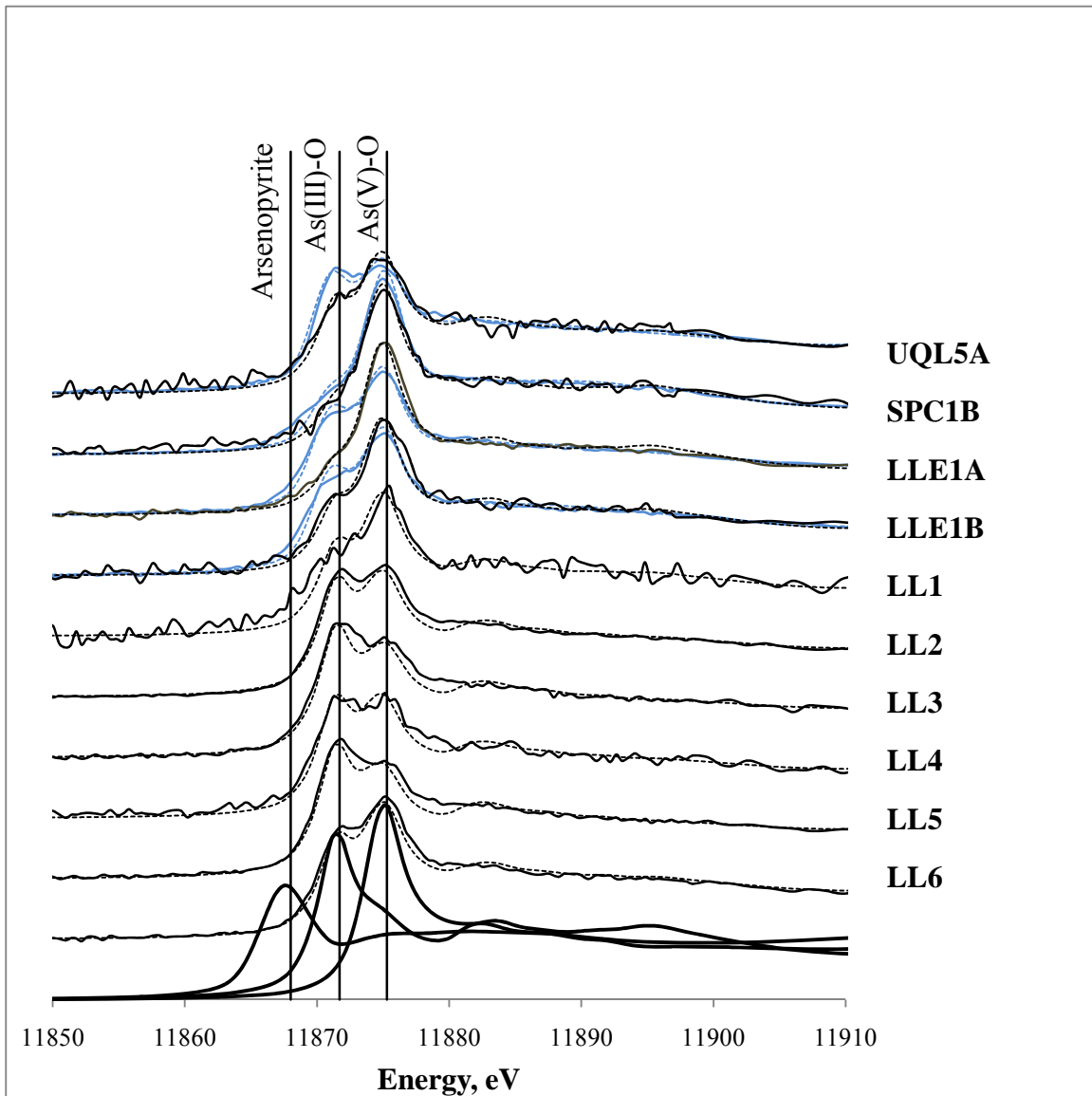
XANES spectra were collected from dried sediments from Long Lake (LL1-6), the settling pond at the northeast corner of Long Lake (LLE1A and B, SPC1B), and one background lake sediment sample from Upper Quinsam Lake (UQL5A). Data for both wet and dried samples were analyzed for a subset of those samples; all results are shown in Figure IV-2 and Table IV-2. Inorganic arsenic bound to oxygen, with the arsenic in both oxidation states +5 and +3, was found to be the predominant arsenic form in all sediments analyzed. No arsenic was found bound to sulphur, suggesting that pyritic

arsenic, the predominant form of arsenic generally found in unoxidized coal, was not present. The current findings are similar to the XANES results from previous studies of contaminated sediments (Gault *et al.*, 2003, Root *et al.*, 2009).

**Table IV-2. Arsenic X-ray absorption near edge structure (XANES) results for wet and dried sediments from the Quinsam watershed. Wet samples are underlined. LL = Long Lake, LLE and SPC = sediments from settling pond and drainage at northeast end Long Lake, UQL = Upper Quinsam Lake**

Sample ID	dry/wet	Total As [ppm]	As(V) %	As(III) %
LL1	dried	36	52	48
LL2	dried	630	35	65
LL3	dried	140	25	75
LL4	dried	110	32	68
LL5	dried	240	24	76
LL6	dried	360	45	55
<u>LLE1A</u>	<u>wet</u>	<u>22</u>	<u>45</u>	<u>55</u>
LLE1A	dried	22	79	21
<u>LLE1B</u>	<u>wet</u>	<u>24</u>	<u>45</u>	<u>55</u>
LLE1B	dried	24	65	35
<u>SPC1B</u>	<u>wet</u>	<u>22</u>	<u>72</u>	<u>28</u>
SPC1B	dried	22	77	23
<u>UQL5</u>	<u>wet</u>	<u>45</u>	<u>36</u>	<u>64</u>
UQL5	dried	45	50	50

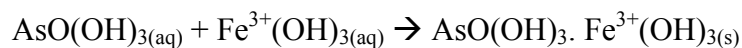
**Figure IV-2. XANES results from Quinsam sediments. Three arsenic standards are shown along the bottom of this figure: arsenopyrite, solid arsenite (As(III)-O) and solid arsenate (As(V)-O). The lowest energy peak of the standards corresponds to the peak that would be observed if pyritic arsenic were present, and is not seen in any of the samples. The first peak, with the lowest energy, found in samples corresponds to an As(III)-O form of arsenic, and the second peak to an As(V)-O form. Solid lines indicate collected data, and dotted lines indicate fit. Blue scans indicate wet sediments.**



Three mine site and one background sediments (LLE1A&B, SPC1B and UQL5A) were analyzed both wet and dry to investigate the effect of sediment drying on arsenic speciation. The same two arsenic species were found in both, but the percentage of As(V)-O was found to increase upon drying by 5 to 34 percent (see Table IV-2 and Figure IV-2). However, a paired t-test did not indicate a significant difference between wet and dried sediments (t-test,  $df = 3$ ,  $t = -2.998$ ,  $p = 0.058$ ). Arsenic oxidation likely took place upon sample drying and storage, and may have included oxidation of dissolved arsenic in pore water. A previous study of dried sediment by XANES found only As(V)-O present (Gault *et al.*, 2003). As(III)-O was found in wet sediments with anthropogenic inputs of arsenic (Root *et al.*, 2009). Root *et al.* identified three redox zones with different arsenic speciation profiles. The first zone was reduced, with arsenic in sulphide phases; the second zone was transitional with As(III)-O and As(V)-O species; and the third zone was oxic, with only As(V)-O. Current data (both wet and dry samples) are similar to data from the transitional zone in the Root study (2009), suggesting the possibility of transitional redox conditions in Quinsam sediments, but source differences must be taken into account when making comparisons.

A t-test of dried sediments indicates that there is significantly more As(V)-O in the mine sediments than in Long Lake sediments (t-test,  $df = 7$ ,  $t = -3.788$ ,  $p = 0.007$ ). The one sediment from Upper Quinsam Lake did not have a significantly different arsenic speciation profile from either Long Lake or the mine pond sediments. These results are not conclusive, as large speciation differences were seen upon drying sediments (see above).

While there is uncertainty in the As(V) and As(III) distributions, the absence of As-S species indicates arsenic that is not in a parent sulphur-mineral form. Instead, the high concentrations of iron within the lake sediments likely act as an arsenic sink, with arsenic (both arsenite As(III)-O and arsenate As(V)-O) binding to iron hydroxides as they precipitate out of the lake water. This process can be represented for arsenate by:



Arsenic can also sorb to solid iron oxyhydroxides in the sediments. As a result, these iron-rich sediments can sequester arsenic, resulting in water above these sediments essentially free of both iron and arsenic.

The iron in coal is present as pyrite,  $\text{FeS}_2$ , and arsenic substitutes sulphur in the pyritic structure (Huggins and Huffman, 1996). Arsenic bound to sulphide phases tend to have the lowest solubility, and are the most commonly found mineral forms of arsenic

(e.g., orpiment  $\text{As}_2\text{S}_3$ , realgar  $\text{As}_4\text{S}_4$  and arsenopyrite  $\text{FeAsS}$ ). As noted previously, arsenic found in sediments in the present study was no longer associated with pyrite but rather more likely associated with iron oxides in lake sediments. The total arsenic concentrations and PCA indicate that if the arsenic was associated with pyrite initially, it has been released from this form and mobilized into the environment.

## **B. Physiologically Based Extraction Test (PBET)**

Long Lake sediments, nearby background lakes, mine site settling pond and drainage ditch sediments, and fine and coarse coal refuse, were subjected to the PBET procedure and the results are presented in Table IV-3. Long Lake sediments had arsenic bioaccessibilities that ranged from 7.9 to 35 percent bioaccessibility (mean = 19 %). Nearby background lakes (including Upper Quinsam Lake, Yellow Point, Wokas Lake and Lower Quinsam Lake) had between 3.8 and 49 percent bioaccessibility (mean = 27 %), sediment samples from the mine site had between 6.1 and 15 percent bioaccessibility (mean = 11 %), and coarse and fine mine refuse had between 23 and 55 percent bioaccessibility (mean = 37 %). Bioaccessibility data from the current study indicate that there is significantly lower arsenic bioaccessibility in the mine site refuse than both Upper Quinsam Lake and No Name Lake sediments (ANOVA,  $F(3, 23) = 4.852$ ,  $p = 0.009$ ; Tukey's test pairwise comparison,  $p = 0.012, 0.022$ ). However, the arsenic solubility in the Long Lake sediments is not significantly different from the background lakes sediment arsenic solubility (Tukey's test pairwise comparison,  $p = 0.95$ ).

**Table IV-3. Arsenic bioaccessibility in selected sediments and coal refuse samples.**

Sample ID	Bioaccessible As %	Total As [ppm]	Bioaccessible As [ppm]
<i>BC Generic Contaminated Sediment Guideline (Sensitive)</i>		<i>11</i>	
<i>BC Generic Contaminated Sediment Guideline (Typical)</i>		<i>20</i>	
<b><i>Long Lake (LL) sediments</i></b>			
LL1	34	<b>36</b>	<i>12</i>
LL2	14	<b>630</b>	<b>88</b>
LL3	15	<b>140</b>	<b>21</b>
LL4	16	<b>110</b>	<i>18</i>
LL5	11	<b>240</b>	<b>26</b>
LL6	7.9	<b>360</b>	<b>28</b>
LL7	35	<b>26</b>	<i>9.1</i>
LL8	18	<b>30</b>	<i>5.4</i>
<b><i>Background lake sediments (Upper Quinsam Lake (UQL), Wokas Lake (WL), Lower Quinsam Lake (LQL) and Yellow Point (LLYP))</i></b>			
UQL1	16	<i>13</i>	<i>2.1</i>
UQL2A	48	<i>4.3</i>	<i>2.1</i>
UQL2B	21	<i>3.9</i>	<i>0.82</i>
UQL3	19	<i>4.5</i>	<i>0.86</i>
UQL4	27	<i>4.7</i>	<i>1.3</i>
UQL5	21	<b>45</b>	<i>9.5</i>
WL1	19	<i>9.1</i>	<i>1.7</i>
LQL1	49	<i>13</i>	<i>6.4</i>
LLYP1	25	<i>0.80</i>	<i>0.20</i>
<b><i>Mine site and coal refuse (sediments from settling pond and drainage at northeast corner of Long Lake (SPC and LLE), coal refuse from 3 South pit access road and coarse and fine refuse provided by the mine (C1-3 and F1-3))</i></b>			
SPC1A	12	<b>21</b>	<i>2.5</i>
SPC1B	6.1	<b>22</b>	<i>1.3</i>
LLE1A	12	<b>22</b>	<i>2.6</i>
LLE1B	15	<b>24</b>	<i>3.6</i>
COAL REFUSE	8.9	<b>21</b>	<i>1.9</i>
C1 (from 2 North pit)	42	<i>4.8</i>	<i>2.0</i>
C2 (from 2 North pit)	30	<i>10</i>	<i>3.0</i>
C3 (from 2 North pit)	55	<i>6.9</i>	<i>3.8</i>
F1	33	<i>6.5</i>	<i>2.1</i>
F2	23	<i>7.0</i>	<i>1.6</i>
F3	38	<i>7.6</i>	<i>2.9</i>

The 2008 report from Golder Associates claims that Long Lake sediment has limited adverse effects on the growth of chironomids and amphipods and states: “The data suggest that the bioavailability of sediment contaminants is likely low, and in these circumstances, reliance on numerical sediment quality data as a predictor of pollution would not provide an adequate characterization of whether or not pollution has occurred.” (Golder, 2008). The Long Lake bioaccessibility data, while not specifically modelling bioavailability to chironomids and amphipods, indicate that the solubility of the sediments is not high (*e.g.*, not above 70 %), but it is also not negligible. Additionally, very low percent bioaccessibilities can still pose a potential risk to receptors if total arsenic concentrations are high (Meunier *et al.*, 2010). The lack of statistically significant differences between Long Lake sediment bioaccessibility and that from other lakes suggests that even though elemental concentrations indicate contamination is likely being introduced by the mine, the form of arsenic in all lake sediments is likely similar, as is suggested by the XANES data. This is not unexpected if the general source of the arsenic is rock weathering and mineral oxidation.

The relatively high bioaccessibility data from the coarse and fine mine waste suggest that arsenic has become more soluble in the wastes than it is in geogenic forms such as arsenopyrite ( $\text{FeAsS}$ , bioaccessibility less than 1 %) (Meunier *et al.*, 2010). This conclusion is supported by the XANES data (our recent X-ray analysis of Long Lake sediments shows a lack of crystalline character). Although the coal refuse analyzed in the present study was very low in arsenic concentration (maximum total arsenic concentration was 10 ppm and maximum bioaccessible arsenic concentration was 3.8 ppm, which is less than the 11 ppm British Columbia interim sediment quality guideline and the 12 ppm Canadian Council of Ministers of the Environment (CCME) guideline for soil), the higher bioaccessibilities (up to 55 %) may be a concern if they are also associated with coal refuse with higher concentrations of arsenic (*e.g.*, material in 4 South pit, south of the middle of Long Lake with high concentrations of arsenic in runoff from test pads).

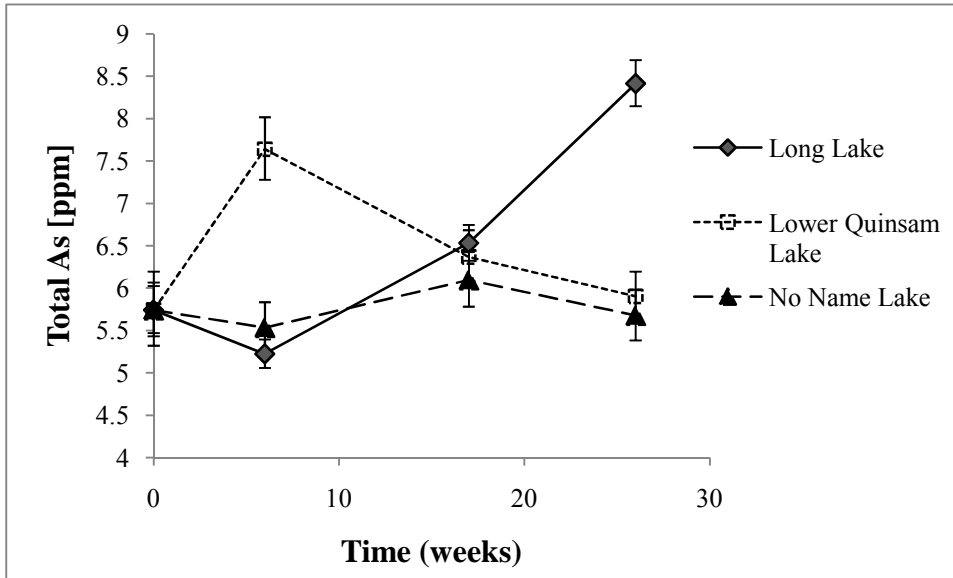
## V. RESULTS FOR PROJECT 2

### A. Caged Mussel Experiment

Marine bivalves such as mussels and oysters are indicators of the environmental health of the local ecosystem (Kwan *et al.*, 2003). In the current study, mussels were used to determine arsenic bioaccumulation and tissue loadings.

The results for total arsenic concentrations in freeze-dried western floater mussel (*Anodonta kennerlyi*) tissues from Lower Quinsam Lake and caged mussels originally located in Lower Quinsam Lake and transported to No Name Lake and Long Lake, are shown in Figure V-1, and data is shown in Table A-3, Appendix A. Statistical analyses were performed using one-way ANOVAs on  $\log_{10}$  transformed mussel tissue arsenic concentrations from each lake against time (including Lower Quinsam Lake  $t = 0$ ), followed by the Dunnett's test to look for differences from  $t = 0$ , to test whether the mussels accumulated different concentrations of arsenic within their tissues over a period of 26 weeks, and whether mussels living in Long Lake and No Name Lake would accumulate more arsenic than those in Lower Quinsam Lake. It was not possible to compare mussels native to Long Lake and No Name Lake, as no mussels were found in these lakes. This may be because of the influence of the local environment, or it may be because fish carrying the glochidia stage of the life cycle of the mussels cannot access these lakes because of the barrier in the Quinsam River about 1 km down river of the exit from Middle Quinsam Lake.

**Figure V-1. Arsenic concentration (ppm dry weight) in western floater mussels (*Anodonta kennerlyi*) over time. Data from all cages for each lake are combined. The error bars shown are the standard error from pooled samples from caged mussels from all cages from each lake.**



The arsenic concentrations in the caged mussels transported from Lower Quinsam Lake and placed in No Name Lake did not change significantly over time (ANOVA,  $F(3, 10)$ , 0.588,  $p = 0.637$ ). Total arsenic analysis for the mussels transplanted to Long Lake did change significantly over time (ANOVA,  $F(3, 16)$ , 39.4,  $p < 0.001$ ) with a significant increase observed by week 26 ( $p < 0.001$ ). This coincides with significantly higher arsenic concentrations in sediments from Long Lake.

The mussel tissue concentrations matched the trends seen in total arsenic concentrations in sediments, contrary to a previous study of caged freshwater mussels where arsenic concentrations in mussel tissues were not correlated with total arsenic concentrations in sediments (Hickey *et al.*, 1995). The similarity in arsenic bioaccessibilities in sediments from Lower Quinsam Lake, No Name Lake and Long Lake is consistent with the current findings where total arsenic concentrations are correlated with uptake levels in mussel tissue.

Mussels from Lower Quinsam Lake have elevated arsenic concentrations compared with the same species measured from another site on Vancouver Island, Yellow Point, where the sediment arsenic concentration is lower (0.8 ppm) and mussel tissues were found to contain 2.7 ppm arsenic.

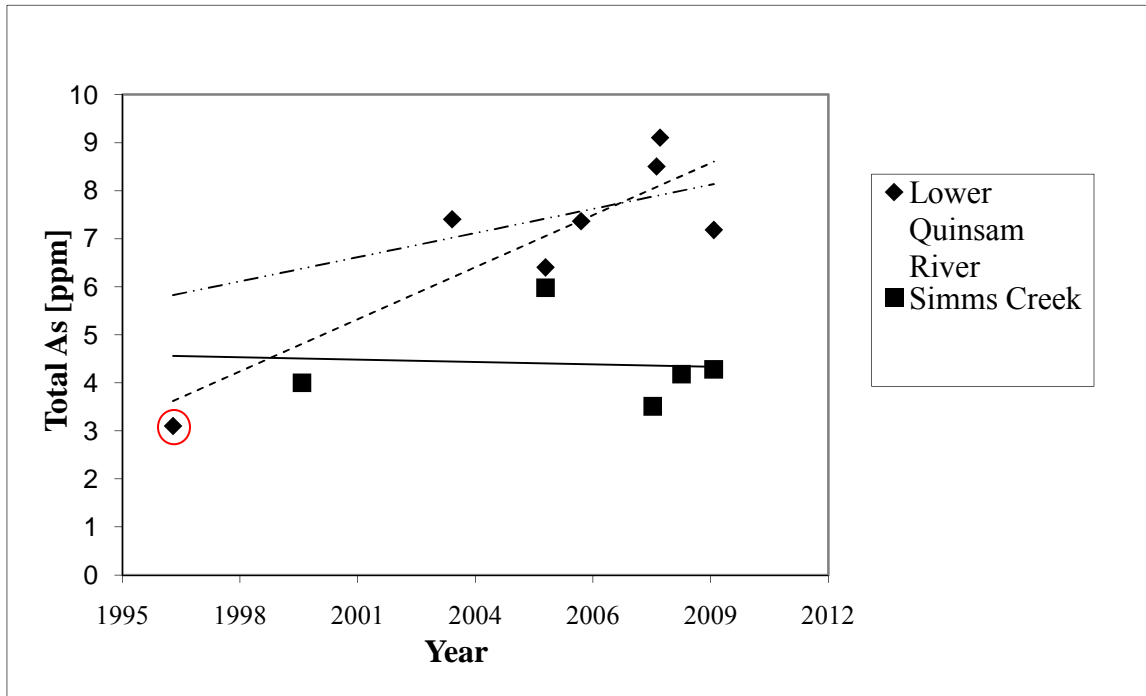
## **B. Long-term monitoring of the Quinsam watershed**

Arsenic concentrations in mussels were measured downriver of Lower Quinsam Lake, in the Quinsam River, and compared with mussels living in the nearby Simms Creek for a period of thirteen years. The black western pearl shell (*Margaritifera falcata*) mussel is commonly found in both of these rivers. Mussels from Quinsam River have elevated arsenic concentrations compared with mussels from Simms Creek (data shown in Figure V-2). The inclusion of a data point from 1997 from the Quinsam River (from Koch *et al.*, 2001), which is lower than the remaining points from the same location from 2003 to 2009 (Figure V-2), results in an apparent increase in mussel arsenic concentrations over time. However, if this influential data point is omitted, mussel tissue arsenic burdens appear steady over time, albeit still elevated compared with Simms Creek. More data would be required to differentiate between these two cases.

Arsenic concentrations vary widely depending upon local geology. Simms Creek mussel arsenic concentrations are again elevated compared with the same species from the relatively pristine environment of the Clearwater River in Washington state, where an arsenic loading of 0.9 ppm arsenic dry weight was reported (Helmstetler and Cowles, 2008).

Similar mussel arsenic concentrations were seen the length of the Quinsam River; samples collected in 2008 upriver and downriver of the hatchery had similar arsenic loading (Table A-5, Appendix A). Arsenic concentrations also do not seem to be caused by sediment contamination as mussels cleaned of sediment were dissected and analyzed with arsenic found in all tissues (Koch *et al.*, 2001).

**Figure V-2. Arsenic concentrations in black western pearl shell (*Margaritifera falcata*) mussels in the Lower Quinsam River and Simms Creek. The solid line shows the least squares fit of Simms Creek data over time. The dotted lines show the least squares fit of data both with and without the data point 1997 (circled in red).**



Overall, these mussels, which were collected a distance from the mine, are not indicating high levels of arsenic concentration with reason for concern for human health, such as was found in marine clams affected by historical gold mining, where arsenic concentrations in softshell clams (*Mya arenaria*) ranged from 220 to 230 ppm wet weight (Koch *et al.*, 2007).

## VI. CONCLUSION

Arsenic concentrations in the current program reflected those collected by Nordin (2006) in 2003/2004 and Golder (2008) during 2007, with the current systematic study providing a larger data set for nearby lakes. The larger data set firmly establishes that Long Lake sediments are significantly higher than surrounding lakes for both arsenic and manganese concentrations, and points to the mine as the source. In other words, the high arsenic concentrations are not a consequence of naturally elevated arsenic in the lake sediments in the region. The high sulphate concentration in the water of Long Lake

(QCC, 2010) is evidence that the processes that release arsenic continue unabated, while the high iron concentrations in the sediment explain how arsenic is being removed from the water column.

The results from Project 1 and Project 2 indicate that arsenic levels are elevated in Long Lake, and are different from nearby unaffected lakes. They also indicate that arsenic is not found as the low solubility geogenic form of pyritic arsenic but rather as an inorganic arsenic oxide. Bioaccessibility tests indicate that arsenic species in the sediments have intermediate arsenic solubilities, and caged mussel studies confirm that more arsenic is being taken up in mussels in Long Lake than in nearby unaffected lakes. Long-term mussel monitoring indicates that arsenic body burdens are slightly higher in the Quinsam River than in Simms Creek. The mussel monitoring does not clearly indicate that arsenic burdens are increasing in the Quinsam River, but further long term monitoring data would confirm whether levels have reached a plateau.

## **VII. USE OF REPORT**

The content of this report is based on information collected during our analysis, our present understanding of methods, and our professional judgment in light of such information available in this report. This report does not provide a legal opinion regarding compliance with applicable laws. The services performed as described in this report were conducted in a manner consistent with that level of care and skill normally exercised by other members of the science and engineering professions currently practicing under similar conditions. The findings and conclusions of this report are valid only as of the date of this report.

## REFERENCES

- British Columbia (2009) Environmental Management Act: Contaminated Sites Regulation, B.C. Reg. 375/96 including amendments up to 343/2008, Schedule 9, Victoria, British Columbia.
- Cullen, W.R. (2008) Is Arsenic an Aphrodisiac? *Royal Society of Chemistry*.
- Forstner, U. and Salomons, W. eds. (1988), *Environmental Management of Solid Waste*. Springer-Verlag Berlin Heidelberg.
- Gault, A.G., Rolya, D.A., Lythgoe, P.R., Farquhar, M.L., Charnock, J.M. and Wogelius, R.A. (2003) Arsenic speciation in surficial waters and sediments in a contaminated waterway: an IC-ICP-MS and XAS based study. *Applied Geochemistry*. 18 1387-1397.
- Golder Associates Ltd. (April 17, 2009) Toxicity testing in support of a site-specific water quality objective for sulphate in Quinsam watershed.
- Golder Associates Ltd. (April 15, 2008) Preliminary sediment quality assessment for Long lake, Quinsam Mine.
- Goldhaber, M.B., Irwin, E.R., Atkins, J.B., Lee, L., Black, D.D., Zappia, H., Hatch, J.R., Pashin, J.C., Sanzolone, R. F., Ruppert, L.F., Kolker, A., and Finkelman, R. B., (2001) Dispersion of Arsenic from arsenic enriched coal and gold ore in the Southern Appalachians <http://wwwbrr.cr.usgs.gov/Arsenic/FinalAbsPDF/goldhaber.pdf>
- Helmstetler, H. and Cowles, D.L. (2008) Population characteristics of native freshwater mussels in the mid-Columbia and Clearwater Rivers, Washington State, *Northwest Science*, 82 (3) 211-221.
- Hickey, C.W., Roper, D.S., and Buckland, S.J. (1995) Metal concentrations of resident and transplanted freshwater mussels *Hyridella menziesi* (Unionacea: Hyriidae) and sediments in the Waikato River, New Zealand. *Science of the Total Environment*. 175 (3) 163-177.
- Huggins F.E. and Huffman G.P. (1996) Comment on and addenda to “Arsenic in coal: A review” by Yudovich and Ketris. *International Journal of Coal Geology* . 66 (1-2) 148-150.
- Koch, I., Reimer, K.J., Beach, A., Cullen, W.R., Gosden, A., and Lai, V.W.-M. (2001) Arsenic speciation in fresh-water fish and bivalves. In W.R. Chappell, C.O. Abernathy and R.L. Calderon (Eds.) *Arsenic exposure and health effects IV* (pp. 115-123). New York: Elsevier.
- Koch, I., McPherson, K., Smith, P. G., Easton, L., Doe, K. G. and Reimer, K. J. (2007) Arsenic bioaccessibility and speciation in clams and seaweed from a contaminated marine environment. *Marine Pollution Bulletin*. 54 (5) 586-594.

- Kwan, K.H. Michael, H. Man Chan, and Y. de Lafontaine. (2003) Metal contamination in zebra mussels (*Dreissena polymorpha*) along the St. Lawrence River. *Environmental Monitoring and Assessment*. 88 (1-3) 193–219.
- Martin, A. J. and Pedersen, T. F. (2004) Alteration to lake trophic status as a means to control arsenic mobility in a mine-impacted lake, *Water research*. 38 4415-4423.
- Meunier, L., Wragg, J., Koch, I. and Reimer, K.J. (2010) Method variables affecting the bioaccessibility of arsenic in soil, *Journal of Environmental Science and Health, Part A*. 45 (5) 517-526.
- Mills, C. (March 2010) Acid Base Accounting (ABA).  
<http://technology.infomine.com/enviromine/ard/Acid-Base%20Accounting/ABAdiscussion.htm>
- Nordin, R. (March 2006), An evaluation of the sediment quality and invertebrate benthic communities of Long lake and Middle Quinsam Lakes with regard to local mining activity, Province of British Columbia Ministry of Environment.
- Ollson, C.A. (2000) Arsenic contamination of the terrestrial and freshwater environment impacted by gold mining operations. M.Sc. RMC.
- Ollson, C.A., Koch, I., Reimer, K.J., Walker, S.R. and Jamieson, H.E. (2001) Characterization of arsenic in solid phase samples collected on the Giant Mine Townsite, Yellowknife, NT. Prepared for the Royal Oak Project Team, Indian and Northern Affairs Canada.
- Ollson, C.A. (2003) Arsenic risk assessments: the importance of bioaccessibility. Ph.D. RMC.
- Price, W.A. and Errington, J.C. (1994), ARD guidelines for mine sites in British Columbia, *Proceedings of the 18th Annual British Columbia Mine Reclamation Symposium* in Vernon, BC.
- Price, W.A., Morin, K. and Hutt, N. (1997), *Guidelines for the Prediction of Acid Rock Drainage and Metal Leaching for Mines in British Columbia: Part II - Recommended Procedures for Static and Kinetic Testing*, Proc. 4th International Conference on Acid Rock Drainage, Vancouver, BC, pp 15-30.
- Quinsam Coal Corporation (2010): Mine Permit Amendment Coarse Coal Rejects Management & 7-South Mining Volume II 7-South Mining.
- Ravel, B. and Newville, M. (2005), ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat*. 12 (4) 537-541.
- Rieberger, K. Metal concentrations in bottom sediment from uncontaminated BC lakes British Columbia. Water Management Division., British Columbia. Ministry of Environment, Lands and Parks. Victoria, B.C.: Water Quality Branch, 1992.

- Rodriguez, R. R.; Basta, N. T.; Casteel, S. W. and Pace, L. W. (1999) An *in vitro* gastrointestinal method to estimate bioavailable arsenic in contaminated soils and solid media. *Environmental Science & Technology*. 33 (4) 642-649.
- Root, R.A., Vlassopoulos, D., Pivera, N.A., Rafferty, M.T., Andrews, C and O'Day, P.A. (2009) Speciation and natural attenuation of arsenic and iron in a tidally influenced shallow aquifer, *Geochemica et Cosmochimica Acta*. 73 (19) 5528-5553.
- Ruby, M. V.; Davis, A.; Schoof, R.; Eberle, S. and Sellstone, C. M. (1996) Estimation of lead and arsenic bioavailability using a physiologically based extraction test. *Environmental Science & Technology*. 30 (2) 422-430.
- Smith, P. G.; Koch, I.; Gordon, R. A.; Mandoli, D. F.; Chapman, B. D. and Reimer, K. J. (2005), X-ray absorption near-edge structure analysis of arsenic species for application to biological environmental samples. *Environmental Science & Technology*. 39 (1) 248-254.
- Sullivan, P. J., Matogod, S. V., and Sobek, A. A. (1986) Dissolution of iron sulfates from pyritic coal wastes. *Environmental Science & Technology*. 20 (10) 1013-1016.



## APPENDIX A: DATA

### LIST OF TABLES

Table A-1: Elemental concentrations of sediments and coal refuse .....	A-2
Table A-2: Factor loadings from Quinsam principal components analysis.....	A-4
Table A-3: Caged mussel experiment: Analytical results for brown western floater mussel ( <i>Anodonata kennerlyi</i> ) .....	A-5
Table A-4: Analytical results for brown western floater mussel ( <i>Anodonata kennerlyi</i> ) located in Simms Creek watershed.....	A-6
Table A-5: Long-term mussel monitoring: Analytical results for black western pearl shell ( <i>Margaritifera falcata</i> ) mussels .....	A-6

**Figure A-1. Elemental loadings from the first two factors of the principal components analysis. Factor 1 explains 30 percent of the total variance in the data set, and Factor 2 explains 28 percent of the total variance.**

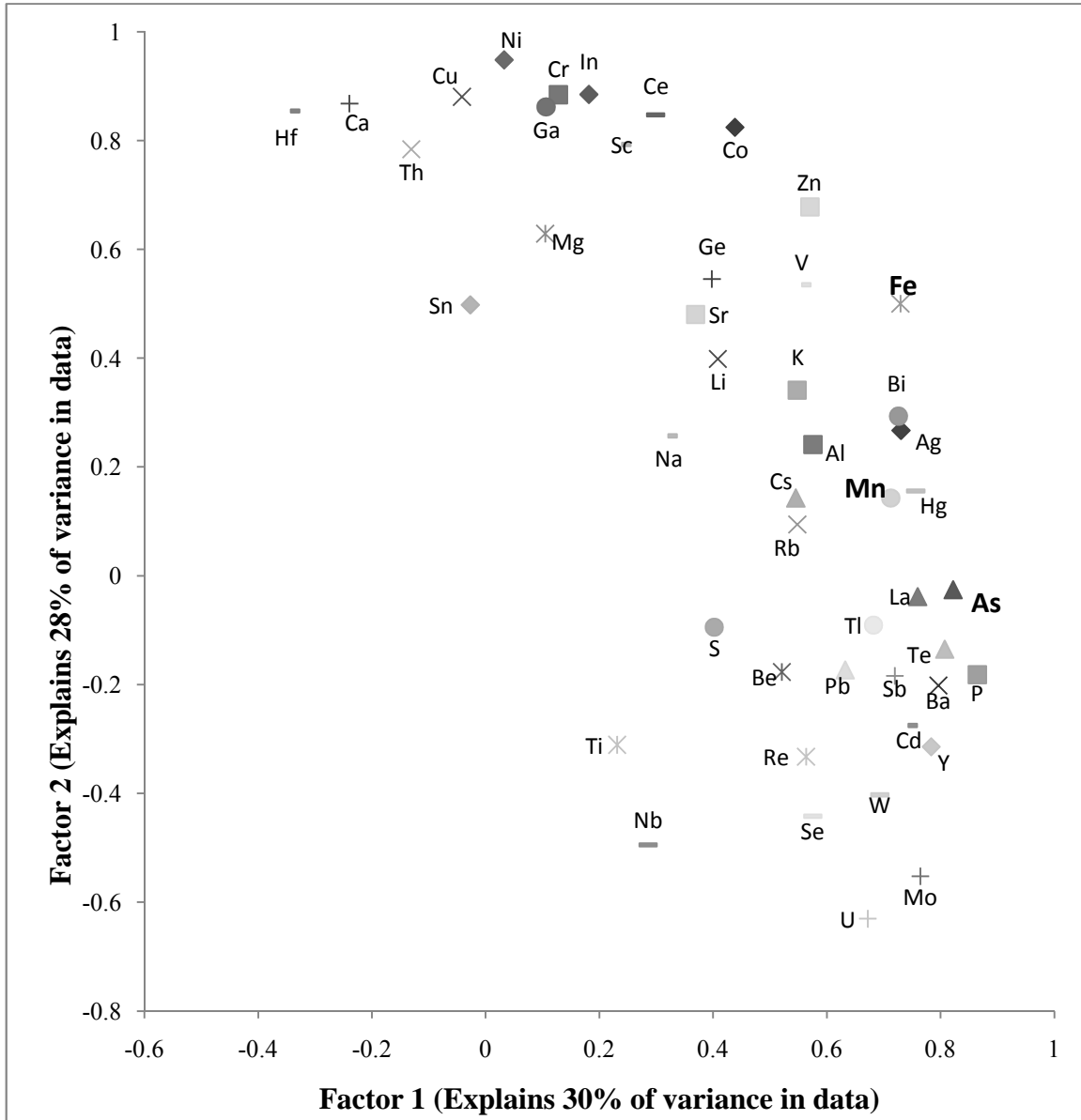


Table A-1. Elemental concentrations of sediments and coal refuse

Sample	Location	Depth m	Ag ppm	Al %	As ppm	Au ppm	B ppm	Ba ppm	Be ppm	Bi ppm	Ca %	Cd ppm	Ce ppm	Co ppm	Cr ppm	Cs ppm	Cu ppm	Fe %	Ga ppm	Ge ppm	Hf ppm	Hg ppm	In ppm	K %
LL1	Long Lake	4.5	0.10	1.3	36	<0.2	10	140	0.22	0.12	1.1	0.37	14	19	29	0.56	52	3.1	4.2	0.05	0.02	0.11	0.03	0.05
LL2	Long Lake	17	0.25	1.8	630	<0.2	10	550	0.24	0.12	0.95	0.50	18	31	36	0.45	51	13	4.6	0.17	0.04	0.27	0.03	0.03
LL3	Long Lake	17	0.26	2.1	140	<0.2	10	210	0.34	0.12	0.86	0.37	20	25	36	0.52	65	9.1	5.0	0.10	0.04	0.31	0.04	0.04
LL4	Long Lake	20-25	0.24	2.2	108	<0.2	<10	90	0.36	0.13	0.85	0.37	20	21	34	0.50	68	8.6	5.5	0.09	0.03	0.29	0.04	0.04
LL5	Long Lake	17	0.23	1.8	240	<0.2	10	160	0.24	0.08	0.92	0.45	17	30	24	0.36	46	14	3.1	0.13	0.06	0.22	0.03	0.03
LL6	Long Lake	15	0.22	1.8	360	<0.2	20	480	0.56	0.11	0.96	0.53	17	28	24	0.37	50	11	4.5	0.08	0.05	0.26	0.03	0.03
LL7	Long Lake	15	0.11	1.4	26	<0.2	20	90	0.24	0.06	0.84	0.30	14	12	31	0.34	60	3.7	4.8	<0.05	0.04	0.11	0.03	0.02
LL8	Long Lake	~5	0.10	1.5	30	<0.2	10	80	0.20	0.05	0.84	0.49	10	14	19	0.27	36	3.0	3.5	0.05	0.03	0.14	0.02	0.02
ML1	Middle Quinsam Lake	3.0	0.07	1.5	9.9	<0.2	<10	80	0.27	0.07	0.80	0.24	9.9	9.2	24	0.32	43	2.1	3.4	0.05	0.02	0.07	0.01	0.02
ML2	Middle Quinsam Lake	3.0	0.08	2.2	34	<0.2	<10	90	0.39	0.08	0.66	0.33	16	15	25	0.56	41	4.0	6.2	0.08	0.05	0.11	0.02	0.03
ML3	Middle Quinsam Lake	3.0	0.07	1.2	8.1	<0.2	<10	50	0.34	0.03	0.75	0.24	11	7.9	22	0.31	62	1.7	3.2	0.07	0.04	0.08	0.007	0.02
ML4	Middle Quinsam Lake	4.0	0.08	1.1	6.5	<0.2	<10	40	0.31	0.03	0.81	0.26	9.9	7.8	24	0.29	73	1.3	2.9	0.07	0.05	0.09	0.005	0.02
ML5	Middle Quinsam Lake	6.0	0.08	1.3	6.7	<0.2	<10	30	0.31	0.02	0.86	0.21	9.5	7.3	27	0.29	72	1.5	2.8	0.07	0.05	0.08	0.005	0.01
ML6	Middle Quinsam Lake	7-8	0.10	1.5	8.5	<0.2	<10	30	0.37	0.04	0.82	0.24	11	8.7	28	0.35	67	2.6	3.4	0.08	0.04	0.12	0.007	0.02
ML7	Middle Quinsam Lake	9.0	0.13	1.8	12	<0.2	<10	50	0.32	0.07	0.84	0.28	11	9.6	26	0.30	56	3.3	3.9	0.09	0.03	0.14	0.01	0.02
ML8	Middle Quinsam Lake	7-8	0.10	1.4	6.5	<0.2	10	40	0.30	0.03	1.1	0.29	11	9.2	29	0.37	74	1.9	3.3	0.08	0.04	0.10	0.008	0.02
ML9	Middle Quinsam Lake	7-8	0.13	2.0	9.2	<0.2	<10	50	0.33	0.06	0.81	0.26	11	10	27	0.33	57	3.4	4.3	0.09	0.03	0.12	0.01	0.02
ML10	Middle Quinsam Lake	2.0	0.09	2.2	6.8	<0.2	<10	80	0.41	0.07	1.1	0.29	14	13	28	0.45	66	2.4	5.8	0.09	0.06	0.09	0.02	0.03
NNL1	No Name Lake	2.0	0.11	0.95	13	<0.2	<10	40	0.28	0.04	0.51	0.48	9.7	8.1	18	0.17	38	1.2	2.1	0.07	0.02	0.11	0.006	0.01
NNL2	No Name Lake	2.0	0.10	1.2	50	<0.2	<10	30	0.23	0.02	0.64	0.45	9.1	15	17	0.14	32	3.9	2.5	0.10	0.02	0.11	0.006	0.01
NNL3	No Name Lake	12	0.27	2.3	55	<0.2	<10	60	0.43	0.07	0.82	0.52	16	20	31	0.29	58	8.0	5.2	0.18	0.05	0.28	0.02	0.02
UQL1A	Upper Quinsam Lake	unknown	0.28	3.3	13	<0.2	<10	40	0.38	0.15	1.4	0.38	16	27	58	0.49	160	5.6	8.7	0.12	0.10	0.19	0.07	0.02
UQL2A	Upper Quinsam Lake	unknown	0.08	3.9	4.3	<0.2	<10	20	0.40	0.04	2.3	0.12	15	28	48	0.34	150	5.7	13	0.20	0.53	0.05	0.05	0.02
UQL2B	Upper Quinsam Lake	unknown	0.08	3.9	3.9	<0.2	<10	20	0.42	0.03	2.3	0.13	15	28	48	0.33	150	5.6	14	0.20	0.61	0.05	0.05	0.02
UQL3A	Upper Quinsam Lake	unknown	0.14	2.7	4.5	<0.2	<10	20	0.32	0.06	1.5	0.29	12	18	36	0.36	97	3.2	7.6	0.11	0.13	0.15	0.04	0.02
UQL4A	Upper Quinsam Lake	unknown	0.13	1.8	4.7	<0.2	<10	10	0.24	0.06	1.2	0.26	9.4	13	32	0.34	89	2.3	4.6	0.08	0.08	0.15	0.03	0.01
UQL5A	Upper Quinsam Lake	unknown	0.27	2.4	45	<0.2	<10	180	0.32	0.16	1.2	0.40	13	33	32	0.35	114	7.7	7.9	0.18	0.07	0.24	0.05	0.02
WL1A	Wokas Lake	unknown	0.10	2.0	9.1	<0.2	<10	50	0.26	0.06	1.2	0.23	9.7	16	26	0.25	76	3.6	5.9	0.12	0.11	0.09	0.03	0.03
LQL1A	Lower Quinsam Lake	unknown	0.03	0.91	13	<0.2	<10	40	0.18	0.03	0.65	0.28	7.7	11	15	0.28	22	1.5	3.5	0.06	0.12	0.04	0.02	0.01
SPC1A	settling pond culvert	unknown	0.11	1.6	21	<0.2	<10	100	0.32	0.09	1.1	0.17	17	23	29	0.69	97	4.8	7.4	0.11	0.06	0.05	0.05	0.09
SPC1B	settling pond culvert	unknown	0.11	1.8	22	<0.2	10	110	0.32	0.09	1.4	0.20	17	23	29	0.67	100	5.0	8.0	0.13	0.08	0.06	0.06	0.12
LLE1A	Long Lake East	unknown	0.11	1.8	22	<0.2	10	70	0.34	0.11	0.95	0.19	18	20	37	0.66	97	4.9	8.5	0.13	0.08	0.07	0.07	0.07
LLE1B	Long Lake East	unknown	0.13	2.2	24	<0.2	10	100	0.39	0.13	0.98	0.18	20	23	39	0.88	99	4.8	10.0	0.12	0.07	0.09	0.08	0.10
C1	2 North coarse refuse, Aug 16-31, 2007	unknown	0.10	1.4	4.8	<0.2	<10	20	0.24	0.04	2.7	0.14	22	31	59	0.28	250	3.9	8.4	0.08	0.33	0.11	0.06	0.02
C2	2 North coarse refuse, Oct 1-15, 2007	unknown	0.10	1.2	10	<0.2	<10	20	0.19	0.05	3.3	0.10	23	28	55	0.25	240	3.5	7.7	0.08	0.31	0.16	0.06	0.02
C3	2 North coarse refuse, Jul 1-15, 2008	unknown	0.09	1.0	6.9	<0.2	<10	20	0.17	0.05	2.7	0.08	22	18	51	0.23	240	2.5	6.7	0.08	0.30	0.05	0.05	0.02
F1	fine refuse, Aug 1-15, 2007	unknown	0.08	1.0	6.5	<0.2	<10	10	0.15	0.04	5.0	0.20	20	23	44	0.21	210	3.7	6.5	0.09	0.30	0.09	0.05	0.02
F2	fine refuse, Sep 16-30, 2007	unknown	0.09	1.1	7.0	<0.2	<10	20	0.18	0.04	3.7	0.16	22	32	45	0.23	220	7.4	6.6	0.13	0.25	0.14	0.06	0.02
F3	fine refuse, Jun 16-30, 2008	unknown	0.08	0.82	7.6	<0.2	10	10	0.15	0.04	4.4	0.11	18	27	40	0.19	220	2.7	5.2	0.09	0.27	0.08	0.05	0.01
COAL REFUSE	3 South pit access road	surface	1.5	1.2	21	<0.2	10	80	0.15	0.24	1.8	1.0	25	42	50	0.37	290	4.7	7.9	0.14	0.22	0.46	0.07	0.02
LLYP1A	Long Lake Yellow Point (Nanaimo)	unknown	0.04	0.70	0.80	<0.2	<10	30	0.20	0.04	0.30	0.05	8.4	2.7	11	0.36	8.6	0.69	2.9	<0.05	0.02	0.01	0.01	0.01

Sample	La ppm	Li ppm	Mg %	Mn ppm	Mo ppm	Na %	Nb ppm	Ni ppm	P ppm	Pb ppm	Rb ppm	Re ppm	S %	Sb ppm	Sc ppm	Se ppm	Sn ppm	Sr ppm	Ta ppm	Te ppm	Th ppm	Ti %	Tl ppm	U ppm	V ppm	W ppm	Y ppm	Zn ppm	Zr ppm
LL1	8.2	11	0.31	1,900	8.1	0.05	0.40	29	710	13	3.6	0.01	1.1	0.35	6.1	0.80	1.2	83	<0.01	0.03	<0.2	0.04	0.06	0.73	72	0.15	16	81	<0.5
LL2	14	7.1	0.20	22,000	21	0.06	0.39	26	4,090	13	2.9	0.002	0.40	0.34	11	2.0	0.50	109	0.01	0.05	0.30	0.04	0.09	0.90	120	0.23	26	74	0.60
LL3	16	11	0.29	4,000	14	0.05	0.49	24	2,420	11	3.6	0.002	0.62	0.34	12	1.9	0.50	84	0.01	0.06	0.30	0.05	0.07	0.91	140	0.24	27	79	0.50
LL4	15	13	0.32	1,200	18	0.05	0.59	22	2,150	11	3.9	0.005	0.59	0.39	12	1.8	0.50	77	<0.01	0.07	0.30	0.05	0.07	0.89	150	0.24	27	80	<0.5
LL5	15	5.2	0.18	3,300	18	0.07	0.41	16	4,160	8.8	2.2	0.001	0.61	0.25	12	2.1	0.40	97	0.01	0.07	0.30	0.04	0.09	0.89	120	0.31	27	69	1.3
LL6	13	16	0.19	28,000	20	0.04	0.36	21	3,730	11	3.1	0.001	0.33	0.28	11	1.8	0.40	128	0.01	0.04	0.30	0.05	0.10	1.1	110	0.26	24	75	0.60
LL7	8.5	16	0.24	600	3.0	0.02	0.39	27	870	7.1	3.5	0.002	0.48	0.27	8.5	1.3	0.50	80	0.01	0.02	0.20	0.02	0.06	0.65	76	0.09	18	56	0.70
LL8	8.5	4.5	0.21	1,500	7.0	0.03	0.46	16	960	5.4	2.1	0.006	0.44	0.21	6.3	1.3	0.20	73	<0.01	0.02	<0.2	0.06	0.07	0.93	85	0.22	20	58	<0.5
ML1	6.8	6.7	0.29	1,700	2.7	0.04	0.52	15	380	6.6	1.8	0.002	0.72	0.15	8.1	1.7	0.20	39	<0.01	0.03	<0.2	0.08	0.02	0.61	69	0.10	13	50	0.70
ML2	9.0	14	0.43	620	3.1	0.03	1.1	19	600	9.6	3.0	0.001	0.60	0.20	8.8	1.7	0.40	38	<0.01	0.03	0.30	0.14	0.05	0.80	100	0.11	16	81	1.5
ML3	9.6	3.4	0.23	330	3.9	0.04	0.61	15	330	4.4	1.8	0.002	0.96	0.12	11	2.7	0.20	39	<0.01	0.02	0.20	0.06	0.02	0.83	62	0.12	19	41	1.2
ML4	9.0	2.3	0.23	340	4.9	0.05	0.57	15	340	3.4	1.7	0.002	0.70	0.22	11	3.1	0.20	37	<0.01	0.01	<0.2	0.05	0.02	0.95	61	0.16	20	29	1.4
ML5	9.2	2.1	0.24	260	4.7	0.04	0.57	14	360	2.1	1.6	0.001	0.64	0.11	11	3.0	<0.2	31	<0.01	0.02	<0.2	0.06	0.02	0.95	68	0.12	20	30	1.6
ML6	9.6	2.4	0.26	420	5.2	0.05	0.63	15	560	4.6	2.0	0.003	0.48	0.14	11	3.2	5.0	35	<0.01	0.03	<0.2	0.06	0.02	1.00	82	0.24	21	35	0.90
ML7	8.3	2.7	0.32	740	5.1	0.07	0.53	13	870	8.5	1.9	0.003	0.45	0.17	9.2	2.9	0.30	48	<0.01	0.05	<0.2	0.07	0.02	0.88	87	0.47	17	45	0.80
ML8	9.9	4.6	0.27	300	4.9	0.27	0.69	15	500	4.2	2.2	0.003	0.57	0.13	12	3.2	0.20	79	0.01	0.02	<0.2	0.07	0.02	0.97	72	0.18	21	42	1.4
ML9	8.4	2.8	0.35	710	4.3	0.08	0.63	13	690	7.4	2.0	0.003	0.35	0.16	9.7	2.5	0.30	44	<0.01	0.04	<0.2	0.08	0.02	0.92	91	0.22	17	43	0.80
ML10	9.1	4.4	0.49	510	2.3	0.06	1.2	18	430	6.1	2.8	0.004	0.60	0.16	12	2.2	0.40	56	0.01	0.02	0.40	0.14	0.02	0.90	96	0.16	18	51	2.1
NNL1	9.1	4.0	0.10	320	4.5	0.01	0.30	14	460	8.5	1.4	0.001	0.34	0.17	5.5	2.0	0.20	24	<0.01	0.03	<0.2	0.03	0.03	0.35	74	0.07	19	44	<0.5
NNL2	8.4	1.4	0.14	310	8.6	0.02	0.52	12	590	4.2	1.1	0.001	0.39	0.16	6.4	1.8	0.20	22	<0.01	0.03	<0.2	0.05	0.03	0.40	110	0.07	17	58	<0.5
NNL3	13	3.5	0.24	930	12	0.02	1.1	15	1,800	7.2	2.0	0.005	0.34	0.24	13	3.4	0.40	52	0.01	0.06	0.20	0.11	0.04	0.76	160	0.17	27	72	1.4
UQL1A	10	4.6	1.1	1,800	3.4	0.02	1.5	37	1,010	9.1	2.2	0.003	0.16	0.28	20	3.6	1.1	35	0.01	0.03	0.20	0.21	0.04	0.53	160	0.25	26	72	4.1
UQL2A	5.9	5.5	1.6	710	0.63	0.04	2.5	49	520	1.5	1.3	0.001	0.05	0.09	15	1.00	0.80	44	0.02	0.01	0.40	0.55	<0.02	0.26	200	0.14	15	71	25
UQL2B	5.8	5.5	1.6	640	0.68	0.04	2.6	50	530	1.3	1.3	0.001	0.05	0.08	15	1.00	0.80	44	0.02	0.01	0.40	0.56	<0.02	0.25	200	0.14	15	72	28
UQL3A	7.3	3.4	0.81	540	1.9	0.03	1.8	27	500	3.5	1.6	0.003	0.16	0.12	14	2.1	0.50	37	0.01	0.01	0.20	0.25	0.03	0.54	130	0.12	19	55	5.6
UQL4A	7.3	2.2	0.50	400	2.3	0.02	1.1	21	430	4.6	1.7	0.003	0.35	0.10	14	2.3	0.30	27	0.01	0.01	<0.2	0.13	0.03	0.43	84	0.13	21	41	3.5
UQL5A	9.6	3.3	0.55	39,000	1.8	0.03	0.58	26	2,240	9.6	1.7	0.002	0.17	0.12	20	3.2	0.50	33	<0.01	0.03	0.20	0.12	0.04	0.61	110	0.19	23	63	2.6
WL1A	6.1	3.1	0.62	890	2.7	0.04	1.6	20	870	5.5	1.8	0.002	0.09	0.13	11	1.4	0.40	35	<0.01	0.02	0.30	0.22	0.03	0.45	110	0.11	13	45	4.8
LQL1A	3.9	3.3	0.26	200	0.54	0.01	0.88	12	270	7.6	2.0	<0.001	0.18	0.16	5.5	0.60	3.3	21	<0.01	<0.01	0.50	0.12	0.05	0.23	55	0.05	8.0	36	5.2
SPC1A	7.6	19	0.67	710	0.69	0.03	0.39	29	550	5.0	7.5	0.001	0.50	0.43	12	0.70	0.70	40	<0.01	0.03	1.3	0.08	0.07	0.39	92	0.08	13	89	1.9
SPC1B	7.9	20	0.74	740	0.79	0.03	0.33	31	570	5.5	8.4	0.001	0.54	0.54	13	0.70	0.50	49	0.01	0.03	1.9	0.09	0.08	0.56	93	0.06	12	88	2.7
LLE1A	7.7	23	0.73	480	0.80	0.03	0.38	31	550	5.2	7.0	0.001	0.47	0.34	13	0.70	0.50	36	<0.01	0.03	1.3	0.06	0.07	0.39	93	0.09	13	95	2.5
LLE1B	8.5	26	0.87	540	0.86	0.04	0.61	34	610	10	9.9	0.001	0.30	0.37	14	0.80	0.60	49	<0.01	0.03	1.4	0.09	0.10	0.49	100	0.10	13	108	2.0
C1	8.6	6.9	0.44	560	0.11	0.06	<0.05	56	210	1.9	1.7	<0.001	0.29	<0.05	19	0.50	1.1	88	<0.01	0.02	0.90	0.007	<0.02	0.08	110	0.06	10	82	4.9
C2	8.7	6.7	0.37	500	0.21	0.06	<0.05	56	180	2.1	1.6	0.001	0.74	<0.05	18	0.70	0.90	97	<0.01	0.01	1.00	0.007	0.03	0.11	94	<0.05	8.6	72	4.9
C3	8.3	4.4	0.30	350	0.13	0.06	<0.05	41	160	2.2	1.4	<0.001	0.15	<0.05	17	0.40	0.90	76	<0.01	<0.01	1.1	0.007	<0.02	0.10	94	<0.05	7.5	56	4.7
F1	7.4	4.5	0.35	580	0.17	0.04	0.05	43	210	1.8	1.3	<0.001	0.26	0.05	16	0.50	0.60	91	<0.01	0.02	0.80	0.006	<0.02	0.08	85	<0.05	9.0	76	4.6
F2	8.1	6.5	0.37	1,600	0.23	0.04	0.05	49	220	1.8	1.4	0.001	0.71	0.07	18	0.60	0.70	72	<0.01	0.01	0.80	0.006	0.02	0.09	100	<0.05	12	79	3.5
F3	6.7	3.6	0.22	340	0.18	0.03	0.05	43	210	2.0	1.00	<0.001	0.29	<0.05	14	0.50	0.60	86	<0.01	0.02	0.80	0.007	<0.02	0.10	81	<0.05	7.1	47	4.7
COAL REFUSE	9.4	5.7	0.45	460	1.1	0.04	0.05	82	220	188	2.0	0.002	2.0	2.9	17	2.5	0.60	58	<0.01	0.02	0.80	0.007	0.21	0.18	95	<0.05	11	241	4.4
LLYP1A	5.3	3.8	0.13	100	0.10	<0.01	0.71	7.1	140	4.1	1.5	<0.001	0.04	0.07	2.3	0.30	0.20	17	<0.01	<0.01	0.30	0.06	0.03	0.19	22	<0.05	5.0	8.0	0.50

**Table A-2. Factor loadings from Quinsam principal components analysis**

Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
Percentage of data variance explained	30	28	11	10	5	4	2
Ag	0.73	0.27	0.19	0.24	-0.41	0.06	0.05
Al	0.58	0.24	-0.75	-0.04	0.02	-0.02	-0.04
<b>As</b>	<b>0.82</b>	<b>-0.03</b>	<b>0.32</b>	<b>0.04</b>	<b>0.09</b>	<b>-0.38</b>	<b>0.06</b>
Ba	0.80	-0.20	0.23	-0.30	0.10	-0.19	-0.03
Be	0.52	-0.18	-0.61	-0.17	0.26	0.07	0.20
Bi	0.73	0.29	0.18	-0.32	-0.25	0.02	-0.21
Ca	-0.24	0.87	0.01	0.34	0.09	0.05	-0.10
Cd	0.74	-0.27	0.16	0.27	-0.41	0.02	0.02
Ce	0.30	0.85	0.30	-0.01	0.15	0.00	0.07
Co	0.44	0.82	0.05	0.13	-0.10	-0.23	0.01
Cr	0.13	0.88	-0.11	0.25	0.04	0.21	-0.10
Cs	0.55	0.14	-0.12	-0.70	0.13	0.28	-0.07
Cu	-0.04	0.88	-0.02	0.32	-0.03	0.28	0.05
<b>Fe</b>	<b>0.73</b>	<b>0.50</b>	<b>-0.02</b>	<b>0.09</b>	<b>0.09</b>	<b>-0.38</b>	<b>0.04</b>
Ga	0.11	0.86	-0.36	-0.26	-0.07	0.03	-0.06
Ge	0.40	0.55	-0.41	0.19	-0.15	-0.14	0.36
Hf	-0.34	0.85	-0.22	0.14	-0.10	-0.07	0.02
Hg	0.76	0.16	0.19	0.52	-0.19	0.03	-0.05
In	0.18	0.88	0.02	-0.28	-0.10	-0.15	-0.17
K	0.55	0.34	0.04	-0.59	0.31	0.20	0.08
La	0.76	-0.04	0.26	0.35	0.25	0.00	0.14
Li	0.41	0.40	0.25	-0.65	0.28	0.02	0.01
Mg	0.10	0.63	-0.64	-0.29	-0.11	0.22	-0.05
<b>Mn</b>	<b>0.71</b>	<b>0.14</b>	<b>0.04</b>	<b>0.13</b>	<b>0.13</b>	<b>-0.44</b>	<b>-0.23</b>
Mo	0.76	-0.55	-0.07	0.24	0.04	-0.02	0.00
Na	0.32	0.26	-0.03	0.39	0.50	0.42	-0.06
Nb	0.29	-0.49	-0.75	-0.24	-0.11	-0.04	-0.03
Ni	0.03	0.95	0.07	0.06	-0.12	0.09	-0.08
P	0.86	-0.18	-0.13	0.06	0.14	-0.39	-0.06
Pb	0.63	-0.17	0.37	-0.18	-0.54	0.13	-0.08
Rb	0.55	0.09	0.13	-0.72	0.20	0.22	0.09
Re	0.56	-0.33	-0.16	0.17	-0.08	0.40	-0.46
S	0.40	-0.09	0.59	0.18	0.05	0.54	0.12
Sb	0.72	-0.18	0.14	-0.35	-0.40	0.21	0.12
Sc	0.24	0.79	-0.21	0.34	0.04	0.21	0.12
Se	0.58	-0.44	-0.30	0.46	-0.19	0.27	0.10
Sn	-0.03	0.50	-0.05	-0.16	-0.11	-0.10	-0.44
Sr	0.37	0.48	0.41	0.27	0.47	-0.03	-0.24
Te	0.81	-0.14	0.14	0.11	0.19	-0.04	0.18
Th	-0.13	0.78	0.22	-0.44	0.05	-0.10	0.24
Ti	0.23	-0.31	-0.85	-0.29	-0.10	-0.06	-0.01
Tl	0.68	-0.09	0.38	-0.43	-0.31	-0.06	0.03
U	0.67	-0.63	-0.24	-0.04	0.16	0.17	-0.02
V	0.56	0.53	-0.43	0.27	0.00	-0.17	0.08
W	0.69	-0.40	-0.45	0.13	0.22	0.02	-0.15
Y	0.78	-0.31	-0.28	0.34	0.09	0.03	0.04
Zn	0.57	0.68	0.17	0.00	-0.18	0.11	0.12
Zr	-0.35	0.70	-0.48	0.01	-0.18	0.04	0.07

**Table A-3. Caged mussel experiment: Analytical results for brown western floater mussel (*Anodonata kennerlyi*).**

Week	Lake	Site	As [ppm]
0	Lower Quinsam Lake		6.08
0	Lower Quinsam Lake		5.41
6	Lower Quinsam Lake		7.08
6	Lower Quinsam Lake		8.23
6	Long Lake	East	5.63
6	Long Lake	East	5.29
6	Long Lake	Center	5.03
6	Long Lake	Center	5.68
6	Long Lake	West	5.00
6	Long Lake	West	4.81
6	No Name Lake	West	5.20
6	No Name Lake	West	5.14
6	No Name Lake	East	6.53
6	No Name Lake	East	5.38
17	Lower Quinsam Lake		6.29
17	Lower Quinsam Lake		6.46
17	Long Lake	East	6.99
17	Long Lake	East	7.19
17	Long Lake	Center	6.35
17	Long Lake	Center	5.92
17	Long Lake	West	6.64
17	Long Lake	West	6.18
17	No Name Lake	West	7.05
17	No Name Lake	West	6.66
17	No Name Lake	East	5.27
17	No Name Lake	East	5.57
26	Lower Quinsam Lake		5.96
26	Lower Quinsam Lake		5.85
26	Long Lake	East	9.34
26	Long Lake	East	9.09
26	Long Lake	Center	7.85
26	Long Lake	Center	8.70
26	Long Lake	West	7.41
26	Long Lake	West	8.26
26	No Name Lake	West	6.05
26	No Name Lake	West	5.84
26	No Name Lake	East	5.28
26	No Name Lake	East	5.54

**Table A-4. Analytical results for brown western floater mussel (*Anodonata kennerlyi*) located in Simms Creek watershed.**

Date	Site	Site ID	As [ppm]
Aug-2009	Yellow Point (Long Lake)	LLYP	2.7

**Table A-5. Long-term mussel monitoring: Analytical results for black western pearl shell (*Margaritifera falcata*) mussels.**

Date	Site	Site ID	As [ppm]
Jan-1997	Lower Quinsam River	QM	3.1
Jan-2000	Simms Creek	SM	4.0
Jul-2003	Lower Quinsam River	QM	7.4
Sep-2005	Lower Quinsam River	QM	6.4
Sep-2005	Simms Creek	SM	6.0
Jul-2006	Lower Quinsam River	QM	7.4
Mar-2008	Simms Creek	SM	3.5
Apr-2008	Lower Quinsam River	QM	8.5
May-2008	Lower Quinsam River, upriver of Quinsam River Hatchery		9.1
Nov-2008	Simms Creek	SM	4.2
Aug-2009	Lower Quinsam River	QM	7.2
Aug-2009	Simms Creek	SM	4.3



## APPENDIX B: QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

### TABLE OF CONTENTS

A. Inorganic Elements in Sediments and Coal Refuse – ALS Environmental, Vancouver, BC.....	B-1
1. Accuracy .....	B-1
2. Precision/Repeatability .....	B-2
B. Arsenic from Bioaccessibility tests – Environmental Sciences Group (ESG), Kingston, ON .....	B-2
1. Accuracy .....	B-2
2. Precision/Repeatability .....	B-2
C. Arsenic in Mussel Tissues – Bill Cullen, University of British Columbia, Vancouver, BC.....	B-3
1. Accuracy .....	B-3
2. Precision/Repeatability .....	B-3

### LIST OF TABLES

Vcdrg"D/3<CNU<T ghgt gpeg'o cvgtkcn't geqxgtkgu'hqt 'ugrgevfg "grgo gpvu(.....)D/6"
Vcdrg"D/4<CNU<Cpcn\ vdecn'Drcpmi'hqt 'ugrgevfg "grgo gpvu(.....)D/7"
Vcdrg"D/5<CNU<Cpcn\ vdecn'f wr rdecv't guwru'hqt 'ugrgevfg "grgo gpvu(.....)D/7"
Vcdrg"D/6<Ctugple'dkqceeguukdkrk\ <Eqptqn'uco r rg'cpf "ur kngu(.....)D/8"
Vcdrg"D/7<Ctugple'dkqceeguukdkrk\ <Cpcn\ vdecn'drcpmi(.....)D/8"
Vcdrg"D/8<Ctugple'dkqceeguukdkrk\ <Cpcn\ vdecn'f wr rdecv't guwru(.....)D/8"
Vcdrg"D/9<Eqptqn'uco r ngu'hqt "cm'bo wuugn'gz vtcevqpu(.....)D/9"
Vcdrg"D/: <Cpcn\ vdecn'drcpmi'hqt "cm'bo wuugn'gz vtcevqpu(.....)D/9"
Vcdrg"D/: <O wuugn'kuuwg'cpcn\ vdecn'f wr rdecv'cpcn\ uku<Eci gf 'o wuugn'gzr gtko gpv(.....)D/: "
Vcdrg"D/32<O wuugn'kuuwg'cpcn\ vdecn'f wr rdecv'cpcn\ uku<Nqpi /vgtto "o wuugn'gzr gtko gpvD/: "



## **APPENDIX B: QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)**

ESG follows an internal quality assurance/quality control program that was implemented to allow data quality to be monitored on an ongoing basis. This program is described in the Quality Assurance Project Plan (QAPP) (ESG, 2009). The points relevant to the discussion of QA/QC sample collection and analysis of monitoring samples in the Quinsam watershed and Simms Creek for the 2010 report are summarized here for completeness.

Accuracy is measured and controlled by instrument calibration, the use of control standards, control spikes and the collection and analysis of blanks.

Control standards and control spikes are reference materials of known concentrations. After analysis of a control standard or spike, the instrument calibration is evaluated based on comparison of the results with the target concentration.

Analytical blanks are processed through extraction/digestion and analysis procedures. These blanks give a measure of the quantity of any contaminant (analyte) that may be added to the overall result during the analysis.

Precision is measured and controlled by the analysis of analytical duplicates. Analytical duplicates are replicate preparations and analyses of the same sample. Comparison of the average relative standard deviations (RSD%) – also known as coefficients of variation, which are calculated as the standard deviation divided by the mean – are used to evaluate laboratory precision. Acceptable limits are generally considered to be less than 40 percent RSD for inorganics and 30 percent for other analyses, with 20 percent or less considered good agreement.

The results of the QA/QC program for the 2010 monitoring sampling program in the Quinsam watershed and Simms Creek are discussed below in order of analysis type. The laboratory associated with each analysis type is also listed.

### **A. Inorganic Elements in Sediments and Coal Refuse – ALS Environmental, Vancouver, BC**

#### *1. Accuracy*

ALS monitored accuracy internally with the analysis of standard reference materials, specifically G2000, GBM3961c, GBM999-5, MRGeo08, and GEOMS-03NRC

(Table B-1). All results for inorganic elements in the measured standards in this study were within control limits (Table B-1).

Analytical blank samples were run with soil batches. Results are presented in Table B-2. All elements in the analytical blanks were below detection limits, with the exception of three blanks which showed iron levels just at the detection limit, and within ALS control limits.

## *2. Precision/Repeatability*

ALS monitored precision internally through the use of analytical duplicates. Three sediment samples were analyzed in duplicate for inorganic elements (Table B-3). The average RSDs for arsenic (9.2 percent), iron (5.6 percent), and manganese (6.0 percent) in the replicates were below 10 percent, indicating very good precision for analysis. All elements and raw data are provided in the attached ALS tables (Appendix A).

## **B. Arsenic from Bioaccessibility tests – Environmental Sciences Group (ESG), Kingston, ON**

### *1. Accuracy*

ESG monitored accuracy internally with the analysis of standard reference materials, specifically NIST2710 (Table B-4). All results for arsenic in the measured standards in this study were within control limits, which were developed in house (Meunier *et al.*, 2010).

Analytical blank samples were run with soil batches. Results are presented in Table B-5. All elements in the analytical blanks were below detection limits. The ICP-MS instrument detection limit was based on three standard deviations of eight replicate measurements of a low concentration solution (1 ppb for arsenic).

### *2. Precision/Repeatability*

Precision was monitored internally through the use of analytical duplicates. Three sediment samples were analyzed in duplicate for arsenic concentrations in phase 1 and 2 (Table B-6). The average RSDs for arsenic for phase 1 (6.6 percent) and phase 2 (7.5 percent) in the replicates were below 10 percent, indicating very good precision for analysis. A matrix spike had excellent recovery (99 and 110 percent recoveries for phase 1 and 2, respectively).



## **C. Arsenic in Mussel Tissues – Bill Cullen, University of British Columbia, Vancouver, BC**

### *1. Accuracy*

Accuracy was monitored internally with the analysis of standard reference materials, specifically DORM-2 (Dogfish muscle) from National Research Council, Canada and *Fucus* sp. reference material (IAEA-140) from International Atomic Energy Agency, Marine Environment Laboratory, Monaco (Table A2-B-7). The total arsenic in DORM-2 was determined to be 19.1 (SD = 0.6) ppm (certified value  $18.0 \pm 1.1$  ppm) and the total arsenic in *Fucus* sp. reference material was 47.2 (SD = 0.5) ppm (certified value 44.3 ppm; 95 percent confidence level range is 42.2 to 46.4 ppm). All results for arsenic in the measured standards in this study were within certified ranges.

Analytical blank samples were run with all batches. All elements in the analytical blanks were below detection limits. The ICP-MS instrument detection limit was based on three standard deviations of eight replicate measurements of a low concentration solution (1 ppb for arsenic).

### *2. Precision/Repeatability*

Precision was monitored internally through the use of analytical duplicates. All caged mussel tissue samples were analyzed in duplicate for arsenic concentrations in mussel tissues (Table B-7). The average RSD for arsenic (5 percent) in the replicates was below 10 percent, indicating very good precision for analysis. Long-term monitoring samples were also analyzed in duplicate (Table B-8). The average RSDs for arsenic (15 percent) in the replicates were below 20 percent, indicating good precision for analysis.



## QUALITY ASSURANCE OVERVIEW

### Laboratory Accreditation and Certification

#### *ISO 17025*

ALS Mineral's North Vancouver and Reno laboratories have received ISO 17025 accreditation from the Standards Council of Canada under CAN-P-4E (ISO/IEC 17025:2005), the General Requirements for the Competence of Testing and Calibration Laboratories, and the PALCAN Handbook (CAN-P-1570).



The scope of accreditation for ALS Minerals Reno includes the following method:

- Au-AA: Determination of Au by Lead Collection Fire Assay and AAS

The scope of accreditation for ALS Minerals Vancouver includes the following methods:

- Au-AA: Determination of Au by Lead Collection Fire Assay and AAS
- Au/Ag-GRA: Determination of Au and Ag by Lead Collection Fire Assay and Gravimetric Finish
- PGM-ICP: Determination of Au, Pt and Pd by Lead Collection Fire Assay and ICP-AES
- ME-ICP41: Multi-Element (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Sr, Ti, Tl, U, V, W, Zn) Determination by Aqua Regia Digestion and ICP-AES
- ME-ICP61: Multi-Element (Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, S, Sb, Sc, Se, Si, Sn, Sr, Ta, Te, Ti, Tl, U, V, W, Y, Zn and Zr) Determination by 4-Acid Digestion and ICP-AES
- ICP81: Al, Co, CU, Fe, Mg, Mn, Ni, Pb, S and Zn by Sodium Peroxide Fusion and ICP-AES
- OG46: Ag, Cu, Pb, and Zn – Determination of Ores and High Grade Material Using ICP-AES Following an Aqua Regia Digestion
- OG62: Ag, Cu, Pb and Zn – Determination of Ores and High Grade Material Using ICP-AES Following a Four-Acid Digestion
- AA45: Ag, Cu, Pb and Zn – Determination of Base Meals Using AAS Following an Aqua Regia Digestion
- AA46: Ag, Cu, Pb, Zn and Mo – Determination of Ores and High Grade materials Using AAS Following an Aqua Regia Digestion
- AA61: Ag, Co, Cu, Ni, Pb and Zn – Determination of Base Metals Using AAS Following a Four-Acid Digestion
- AA62: Ag, Co, CU, Mo, Ni, Pb and Zn – Determination of Ores and High Grade Materials Using AAS Following a Four-Acid Digestion

Our Val d'Or, Quebec lab is actively pursuing ISO 17025 accreditation for Au by Fire Assay methods.

## **ISO 9001**



ALS Minerals laboratories in North America are registered to ISO 9001:2008 for the “provision of assay and geochemical analytical services” by QMI-SAI Global Quality Registrars.

The ISO 9001: 2008 registration provides evidence of a quality management system covering all aspects of our organization. ISO 17025 accreditation provides specific assessment of our laboratory’s analytical capabilities. In our opinion, the combination of the two ISO standards provides our clients complete assurance regarding the quality of every aspect of ALS Minerals operations.

Aside from laboratory accreditation, ALS Minerals has been a leader in participating in, and sponsoring, the assayer certification program in British Columbia. Many of our analysts have completed this demanding program that includes extensive theoretical and practical examinations. Upon successful completion of these examinations, they are awarded the title of Registered Assayer.

## **Quality Assurance Program**

The quality assurance program is an integral part of all day-to-day activities at ALS Minerals and involves all levels of staff. Responsibilities are formally assigned for all aspects of the quality assurance program.

### ***Sample Preparation Quality Specifications***

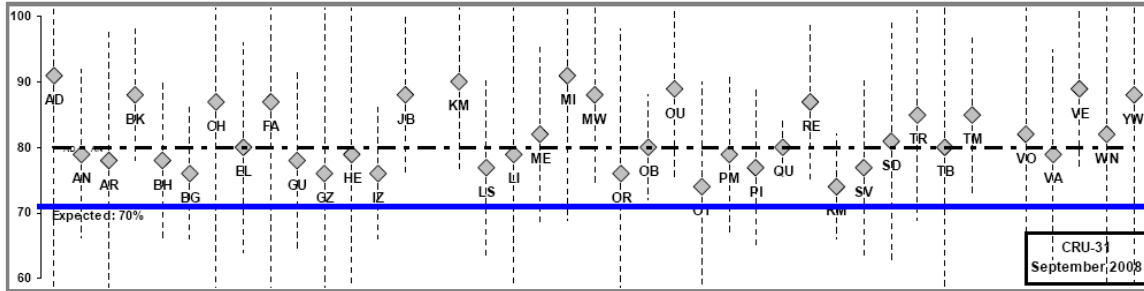
Standard specifications for sample preparation are clearly defined and monitored. The specifications for our most common methods are as follows:

- **Crushing (CRU-31)**  
> 70% of the crushed sample passes through a 2 mm screen
- **Ringing (PUL-31)**  
> 85% of the ring pulverized sample passes through a 75 micron screen (Tyler 200 mesh)
- **Samples Received as Pulps**  
>85% of the sample passes through a 75 micron screen (Tyler 200 mesh)

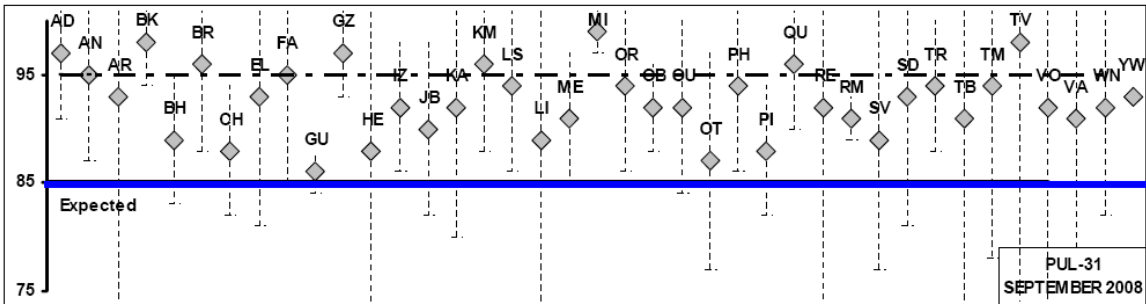
These characteristics are measured and results reported to verify the quality of sample preparation. Our standard operating procedures require that samples at every preparation station are tested regularly throughout each shift. Measurement of sample preparation quality allows the identification of equipment, operators and processes that are not operating within specifications.

QC results from all global sample preparation laboratories are captured by the LIM System and the QA Department compiles a monthly review report for senior management on the performance of each laboratory from this data.

## CRU-31



## PUL-31



### *Other Sample Preparation Specifications*

Sample preparation is a vital part of any analysis protocol. Many projects require sample preparation to other specifications, for instance >90% of the crushed sample to pass through a 2 mm screen. These procedures can easily be accommodated and the Prep QC monitoring system is essential in ensuring the required specifications are routinely met.

### ***Analytical Quality Control – Reference Materials, Blanks & Duplicates***

The LIMS inserts quality control samples (reference materials, blanks and duplicates) on each analytical run, based on the rack sizes associated with the method. The rack size is the number of sample including QC samples included in a batch. The blank is inserted at the beginning, standards are inserted at random intervals, and duplicates are analysed at the end of the batch. Quality control samples are inserted based on the following rack sizes specific to the method:

<b>Rack Size</b>	<b>Methods</b>	<b>Quality Control Sample Allocation</b>
20	Specialty methods including specific gravity, bulk density, and acid insolubility	2 standards, 1 duplicate, 1 blank
28	Specialty fire assay, assay-grade, umpire and concentrate methods	1 standard, 1 duplicate, 1 blank
39	XRF methods	2 standards, 1 duplicate, 1 blank
40	Regular AAS, ICP-AES and ICP-MS methods	2 standards, 1 duplicate, 1 blank
84	Regular fire assay methods	2 standards, 3 duplicates, 1 blank

Laboratory staff analyse quality control samples at least at the frequency specified above. If necessary, they may include additional quality control samples above the minimum specifications.

All data gathered for quality control samples – blanks, duplicates and reference materials – are automatically captured, sorted and retained in the QC Database.

### ***Quality Control Limits and Evaluation***

Quality Control Limits for reference materials and duplicate analyses are established according to the precision and accuracy requirements of the particular method. Data outside control limits are identified and investigated and require corrective actions to be taken. Quality control data is scrutinised at a number of levels. Each analyst is responsible for ensuring the data submitted is within control specifications. In addition, there are a number of other checks.

### ***Certificate Approval***

If any data for reference materials, duplicates, or blanks falls beyond the control limits established, it is automatically flagged red by the computer system for serious failures, and yellow for borderline results. The Department Manager(s) conducting the final review of the Certificate is thus made aware that a problem may exist with the data set.

### ***Precision Specifications and Definitions***

Most geochemical procedures are specified to have a precision of  $\pm 10\%$ , and assay procedures  $\pm 5\%$ . The precision of Au analyses is dominated by the sampling precision.

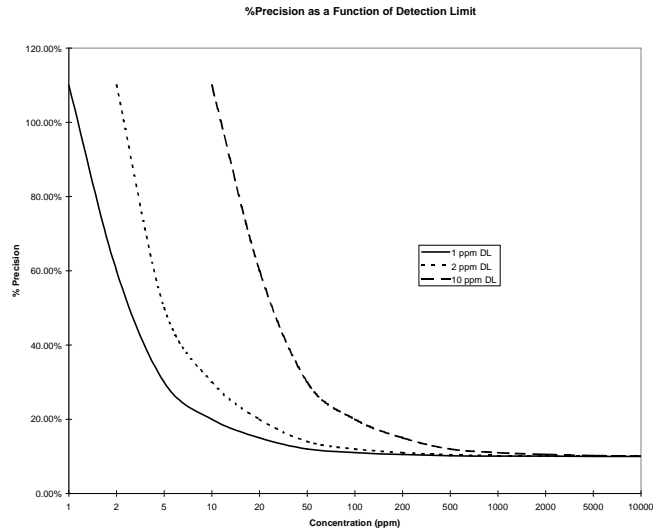
Precision can be expressed as a function of concentration:

$$P_c = \left( \frac{\text{DetectionLimit}}{c} + P \right) \times 100\%$$

- where  $P_c$  - the precision at concentration  $c$   
 $c$  - concentration of the element  
 $P$  - the "Precision Factor" of the element. This is the precision of the method at very high concentrations, i.e. 0.05 for 5%.

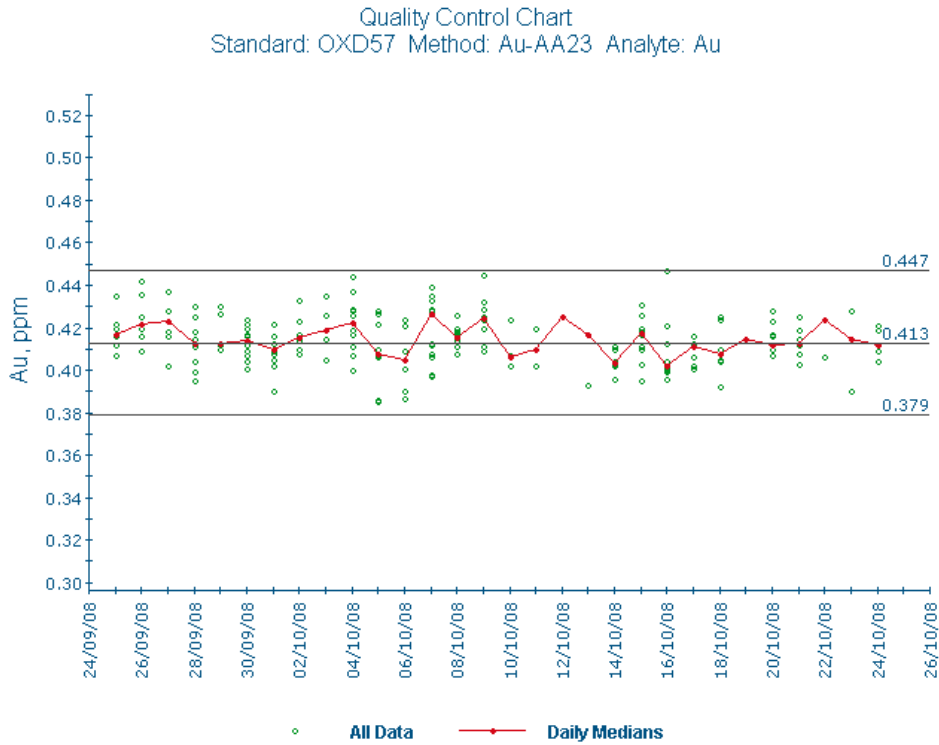
(M. Thompson, 1988. Variation of precision with concentration in an analytical system. Analyst, 113: 1579-1587.)

As an example, precision as a function of concentration (10% precision) is plotted for three different detection limits. The impact of detection limit on precision of results for low-level determinations can be dramatic.



### ***Evaluation of Trends***

Control charts for frequently used method codes are generated and evaluated by laboratory staff on a regular basis. The control charts are evaluated to ensure internal specifications for precision and accuracy are met. The data is also reviewed for any long-term trends and drifts.



### ***External Proficiency Tests***

Proficiency testing provides an independent assessment of laboratory performance by an outside agency. Test materials are regularly distributed to the participants and results are processed by a central agency. The results are usually converted to a Z-Score to rate the laboratory's result against the consensus value from all participating labs.

All ALS Minerals analytical facilities in North America participate in proficiency tests for the analytical procedures routinely done at each laboratory. ALS Minerals has participated for many years in proficiency tests organized by organizations such as Canadian Certified Reference Materials Projects, and Geostats as well as a number of independent studies organized by consultants for specific clients. We have participated also participated in several certification studies for new certified reference materials by CANMET and Rocklabs.

Feedback from these studies is invaluable in ensuring our continuing accuracy and validation of methods.

### ***Quality Assurance Meetings***

A review of quality assurance issues is held regularly at Technical and Quality Assurance Meetings. The meetings cover such topics as:

- Results of internal round robin exchanges, external proficiency tests and performance evaluation samples
- Monitoring of control charts for reference materials
- Review of quality system failures
- Incidents raised by clients
- Results of internal quality audits
- Other quality assurance issues

The Quality Assurance Department and senior laboratory management participate in these meetings.



**Table B-1 Standard Reference Material Elemental Recoveries**

<b>Standard Reference Material</b>	<b>As [ppm]</b>	<b>Fe [ppm]</b>	<b>Mn [ppm]</b>
G2000	473	3.77	549
	466	3.73	552
Average recovery	470	3.75	551
Std Dev	5	0.03	2
Control Limits	436-533	3.41-4.19	506-630
GBM3961c	737	7.34	624
	780	8.07	706
	743	7.59	669
	733	7.72	671
	740	7.38	645
Average recovery	747	7.62	663
Std Dev	19	0.30	31
Control Limits	669-817	7.14-8.75	592-734
GBM999-5	3.5	2.79	58
Control Limits	2.7-3.5	2.56-3.15	49-71
MRGeo08	31.8	3.51	402
	33.4	3.7	424
Average recovery	32.6	3.61	413
Std Dev	1.1	0.13	16
Control Limits	28.9-35.5	3.38-4.15	398-498
GEOMS-03	608	3.94	527
	608	4.08	548
	611	3.86	520
Average recovery	609	3.96	532
Std Dev	2	0.11	15
Control Limits	553-677	3.48-4.28	483-601

**Table B-2 Blank Elemental Recoveries**

<b>Standard Reference Material</b>	<b>As [ppm]</b>	<b>Fe [ppm]</b>	<b>Mn [ppm]</b>
Blank	<0.1	0.01	<5
	<0.1	0.01	<5
	<0.1	<0.01	<5
	<0.1	<0.01	<5
	<0.1	<0.01	<5
	<0.1	<0.01	<5
	<0.1	0.01	<5
<b>Control Limits</b>	<b>&lt;0.1-0.2</b>	<b>&lt;0.01-0.02</b>	<b>&lt;5-10</b>

**Table B-3 Duplicate Analyses**

<b>Duplicate Analyses</b>	<b>As [ppm]</b>	<b>Fe [ppm]</b>	<b>Mn [ppm]</b>
LL5	243	13.7	3290
duplicate	233	14.3	3170
Rel Std Dev (%)	3.0	3.0	2.6
LL6	361	11.1	28400
duplicate	403	12.05	30700
Rel Std Dev (%)	7.8	5.8	5.5
ML10	6.8	2.36	512
duplicate	6	2.26	480
Rel Std Dev (%)	8.8	3.1	4.6
<b>Average Rel Std Dev (%)</b>	<b>6.5</b>	<b>4.0</b>	<b>4.2</b>

**Table B-4. Arsenic bioaccessibility:  
 Control sample and spikes**

	<b>Phase 1 %</b>	<b>Phase 2 %</b>
NIST 2710	41.90	43.51
	38.40	33.31
	46.00	44.00
	35.98	34.63
<b>Average recovery</b>	<b>40.57</b>	<b>38.86</b>
<b>Std Dev</b>	<b>4.36</b>	<b>5.68</b>
Control Limits	24 - 57	23 - 49
Spike recovery (%)	99	110.0
Control Limits	80-120	80-120

**Table B-5. Arsenic bioaccessibility: Analytical blanks**

<b>Sample</b>	<b>Phase 1 [ppm]</b>	<b>Phase 2 [ppm]</b>
Blank	<30	<30
Blank	<30	<30
Blank	<0.5	<0.5
Blank	<0.5	<0.5

**Table B-6. Arsenic bioaccessibility analytical duplicate results**

<b>Sample</b>	<b>Phase 1 %</b>	<b>Phase 2 %</b>
LL8	18.2	13.6
duplicate	16.1	15.3
Std Dev	1.5	1.2
Rel Std Dev (%)	8.5	8.0
SPC1B	5.21	6.49
duplicate	5.06	5.62
Std Dev	0.10	0.61
Rel Std Dev (%)	2.0	10
C3	51.2	56.8
duplicate	44.9	53.5
Std Dev	4.5	2.3
Rel Std Dev (%)	9.4	4.2
<b>Average Rel Std Dev (%)</b>	<b>6.6</b>	<b>7.5</b>



**Table B-7. Control samples for all mussel extractions**

Sample	As [ppm]
DORM-2	19.2
	18.9
<b>Average recovery</b>	<b>19.1</b>
<b>Std Dev</b>	<b>0.2</b>
Certified Value	16.9-19.1
<i>Fucus</i> sp. RM	46.8
	47.5
<b>Average recovery</b>	<b>47.2</b>
<b>Std Dev</b>	<b>0.5</b>
Control Limits	42.2-46.4

**Table B-8. Analytical blanks for all mussel extractions**

Sample	As [ppm]
Blank	0.004
Blank	0.003

**Table B-9. Mussel tissue analytical duplicate analysis: Caged mussel experiment**

Sample	As [ppm]	Sample	As [ppm]
LQL-t0-1	6.1	LL-West-t4m-1	6.6
duplicate	5.4	duplicate	6.2
Std Dev	0.5	Std Dev	0.3
Rel Std Dev (%)	8.2	Rel Std Dev (%)	5.1
LQL-t6w-1	7.1	NNL-West-t4m-1	7.1
duplicate	8.2	duplicate	6.7
Std Dev	0.8	Std Dev	0.3
Rel Std Dev (%)	11	Rel Std Dev (%)	4.0
LL-East-t6w-1	5.6	NNL-East-t4m-1	5.3
duplicate	5.3	duplicate	5.6
Std Dev	0.2	Std Dev	0.2
Rel Std Dev (%)	4.3	Rel Std Dev (%)	4.0
LL-Center-t6w-1	5.0	LQL-t6m-1	6.0
duplicate	5.7	duplicate	5.8
Std Dev	0.5	Std Dev	0.1
Rel Std Dev (%)	8.5	Rel Std Dev (%)	1.4
LL-West-t6w-1	5.0	LL-East-t6m-1	9.3
duplicate	4.8	duplicate	9.1
Std Dev	0.1	Std Dev	0.2
Rel Std Dev (%)	2.8	Rel Std Dev (%)	1.9
NNL-West-t6w-1	5.2	LL-Center-t6m-1	7.9
duplicate	5.1	duplicate	8.7
Std Dev	0.04	Std Dev	0.6
Rel Std Dev (%)	0.8	Rel Std Dev (%)	7.2
NNL-East-t6w-1	6.5	LL-West-t6m-1	7.4
duplicate	5.4	duplicate	8.3
Std Dev	0.8	Std Dev	0.6
Rel Std Dev (%)	14	Rel Std Dev (%)	7.7
LQL-t4m-1	6.3	NNL-West-t6m-1	6.1
duplicate	6.5	duplicate	5.8
Std Dev	0.13	Std Dev	0.1
Rel Std Dev (%)	2.0	Rel Std Dev (%)	2.5
LL-East-t4m-1	7.0	NNL-East-t6m-1	5.3
duplicate	7.2	duplicate	5.5
Std Dev	0.1	Std Dev	0.2
Rel Std Dev (%)	2.0	Rel Std Dev (%)	3.5
LL-Center-t4m-1	6.4	<b>Average Rel Std Dev (%)</b>	<b>5.0</b>
duplicate	5.9		
Std Dev	0.3		
Rel Std Dev (%)	5.0		

**Table B-10. Mussel tissue analytical duplicate analysis: Long-term mussel experiment**

Sample	Date	As [ppm]	Sample	Date	As [ppm]
Lower Quinsam River	Sep-05	5.1	Simms Creek	Nov-08	4.4
duplicate		7.5	duplicate		4.0
Std Dev		1.7	Std Dev		0.3
Rel Std Dev (%)		28	Rel Std Dev (%)		6.8
Simms Creek	Sep-05	5.5	Lower Quinsam River	Aug-09	8.3
duplicate		6.4	duplicate		6.0
Std Dev		0.6	Std Dev		1.6
Rel Std Dev (%)		10	Rel Std Dev (%)		22
Lower Quinsam River	Jul-06	8.0	Simms Creek	Aug-09	5.0
duplicate		6.7	duplicate		3.6
Std Dev		0.9	Std Dev		1.0
Rel Std Dev (%)		13	Rel Std Dev (%)		22
Simms Creek	Mar-08	3.0	<b>Average Rel Std Dev (%)</b>		<b>15</b>
duplicate		4.0			
Std Dev		0.7			
Rel Std Dev (%)		19			
Lower Quinsam River	Apr-08	9.7			
duplicate		7.3			
Std Dev		1.7			
Rel Std Dev (%)		20			
Quinsam River, above hatchery	May-08	9.3			
duplicate		9.0			
Std Dev		0.2			
Rel Std Dev (%)		2.3			
Middle Quinsam River, inlet	Jun-08	7.6			
duplicate		8.7			
Std Dev		0.8			
Rel Std Dev (%)		9.5			



## **APPENDIX C: ACID ROCK DRAINAGE (ARD) AND ARSENIC CYCLING**

### **LIST OF TABLES**

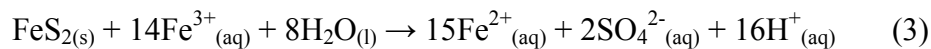
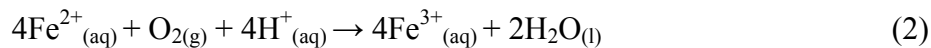
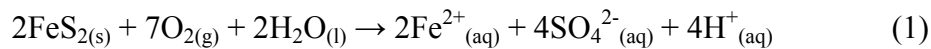
Table C-1: Net Potential Ratio (NPR) screening criteria (adapted from Price <i>et al.</i> , 1997) .....	C-3
Table C-2: Selected data from the 7 South strata (adapted from QCC, 2010) .....	C-5

## APPENDIX C: ACID ROCK DRAINAGE (ARD) AND ARSENIC CYCLING

Acid rock drainage (ARD), sometimes referred to as acid mine drainage in mining situations, is a concern at Long Lake. Water flows into the lake from a number of industry-affected sources, including seep water from the southwest portion of the lake, a settling pond to the east of the northern tip of the lake, drainage from ditches near the settling ponds via culverts, and a quarry north of the north end of the lake.

The flow of acidic water from rock, generally containing high metal and metalloid concentrations including arsenic, is caused by oxidation, and is influenced by the relative amounts of water and oxygen available, the presence of carbonate minerals to neutralize acidification processes and the physical characteristics of mining waste, including the particle size and the hydrologic regime (Forstner and Salomons, 1988). Intermittent exposure to water is believed to enhance ARD processes.

Arsenic mobilization of pyrite associated arsenic is through oxidation and can be represented by the following set of equations:



The oxidation of pyrite can be represented by the spontaneous reactions shown in equations 1 - 3. Step two is extremely slow but can be accelerated by microbial catalysis such as by *Thiobacillus ferrooxidans*, increasing the overall rate of pyrite oxidation. When pyrite is oxidized by Fe(III) (Equation 3), the products are Fe(II), sulphate and more acidity (Sullivan *et al.*, 1986). This resulting acidity can dissolve metals in the matrix such as copper, nickel, lead aluminum and manganese. Any arsenic in pyrite is released as water soluble species — mainly arsenate — during the oxidation.

Equations 4 and 5 show how mobilized iron and arsenic is precipitated out of the water column. Step 4 shows the generation of insoluble ferric hydroxide which forms under appropriate pH conditions. Arsenate can then be removed from solution by co-precipitation with the ferric hydroxide, if and when the precipitate forms, Equation 5. Iron oxyhydroxides, a common component of freshwater sediments, play an important role in sequestering dissolved arsenic in both lake and river environments similar to Equation 5. Rapid adsorption of soluble arsenic species onto iron oxyhydroxides is supported by laboratory studies; the rate of adsorption is fast (minutes) and the rate for As(V) is faster than As(III) (Gault *et al.*, 2003).

Arsenic sorbed to iron oxides is released to pore waters depending upon the depth of reductive dissolution of Fe(III) oxyhydroxides and hence on the oxidation rate of organic matter. Sediments characterized by a relatively low oxygen demand and a correspondingly thick zone of oxic sediments have a greater capacity to resorb diffusing arsenic, thereby limiting the diffusive transport of arsenic into bottom waters. Conversely, in sediments with a greater oxygen demand, the efficiency of scavenging mechanisms is significantly reduced resulting in a greater flux of arsenic to the water column.

The loading of algal nutrients in contaminated systems has the potential to amplify the release of sediment-derived arsenic via alteration of the sedimentary redox conditions. High concentrations of phosphorus and nitrogen, as could come from anthropogenic activities, increases primary production and the downward flux of organic matter associated with lake eutrophication, which in turn influences the oxygen demand at the water sediment interface (Martin and Pedersen, 2004). This is similar to the mechanism responsible for arsenic release to groundwater in Bangladesh for arsenic-rich sediments.

The acid producing potential of wastes can be evaluated using acid base accounting (ABA). This is measured using the Sobek ratio, or net (or neutralization) potential ratio (NPR): NP/AP, where NP is the neutralization potential (an estimate of the ability of the material to neutralize acid produced by the oxidative process) and AP is the acid generating potential. This method does not address the release of chemical species such as sulphate accompanied by soluble forms of metals and metalloids such as arsenic, copper, and manganese. Materials with an NPR less than one are likely to be an acid drainage source, unless the sulphide content is very low and/or there are significant slow

release, non-carbonate sources of alkalinity (Price and Errington, 1994). There is no consensus that an NPR of 2 eliminates potential for ARD (a benchmark used by QCC) as research suggests that the acid drainage potential will be considered uncertain if materials have a NPR of less than 4 creating a “grey zone” for NPRs of between 1 and 4 (Price *et al.*, 1997). This grey zone is greatly influenced by the presence of sulphides as seen in Table II-1.

**Table C-1: Net Potential Ratio (NPR) Screening Criteria (adapted from Price *et al.*, 1997)**

Potential for Acid Rock Drainage	NPR Screening Criteria	Comments
Likely	< 1	
Possibly	1 – 2	Possible if NP is insufficiently reactive or is depleted at a faster rate than sulphides
Low	2 – 4	Possible if significant preferential exposure of sulphides along fracture planes, or extremely reactive sulphides in combination with insufficiently reactive NP
None	> 4	No further testing required unless materials are to be used as a source of alkalinity

The ABA method is a static procedure and provides no information on the speed, or kinetic rate, with which acid generation or neutralization proceeds (Mills, 2010). The NPR gives no information on the rate of the oxidative chemical process that will *inevitably* take place once material is exposed to air.

At Quinsam Coal, the refuse contains up to 1.57 percent sulphur (up to 1.30 percent pyritic sulphur and 0.15 percent sulphate). The NPR ranges between 2.47 – 107 for coarse refuse and 3.26 – 32.03 for fine refuse. The QCC defines material with a NPR greater than 2 as having no potential to generate acid. All fine residues and coarse residues with a NPR of < 2 are stored underwater in a tailings pond at 3 South pit (QCC,



2010). Coarse residues are also used for road construction and to build the walls of containment ponds. Related material has been dumped south of Long Lake. These materials, no matter how they are classified, all have the potential to oxidize and mobilize sulphate, arsenic, iron, manganese as well as other metal and metalloids into the surrounding environment leading to elevated arsenic and manganese concentration in sediments (Goldhaber *et al.*, 2001). Table C-2 includes data from a different area not discussed in the current report, and shows how arsenic is distributed in the area.

Finally, a rock quarry, established in 1995, is located on the north side of Long Lake and drains into Long Lake. This quarry contains mostly material with a NPR > 2. Material with a NPR less than 2 is treated as potentially acid generating, but the remaining material could be contributing to elevated arsenic and iron levels in Long Lake.

**Table C-2: Selected data from the 7 South strata (adapted from QCC, 2010)**

Sample No.	Sample Information	Lithology	Sample Interval		Total Thickness (m)	As [ppm]	Fe %	Mn [ppm]	S %
			From (m)	To (m)					
Hole QU-0707-C			<i>Average Crustal Abundance</i>			1.8	5.63	950	0.035
0707-ARD1		Sandstone	9.65	10.33	0.68	25	1.33	634	0.97
0707-ARD2		Sandstone	10.33	12.99	2.66	63	2.74	271	2.22
0707-ARD3	No.5 Roof	Sandstone	12.99	13.89	0.90	89	4.65	429	4.25
0707-ARD4	No. 4 Floor	Mudstone-Sandstone			0.00	56	5.25	522	4.17
Hole QU-07-09-C									
0709-1		Sandstone	4.67	6.76	2.1	11	3.28	119	0.01
0709-2		Sandstone	6.76	9.94	3.2	16	3.96	140	0.01
0709-3		Sandstone	9.94	13.36	3.2	7	1.38	68	0.03
0709-4		Sandstone	13.36	18.73	5.4	7	2.36	264	0.02
0709-5		Sandstone	18.69	22.87	4.2	21	3.14	604	0.24
0709-6		Sandstone	22.87	25.54	2.7	110	6.58	672	4.31
0709-7	No. 5 Roof	Sandstone/Mudstone	25.54	26.82	1.3	93	5.34	469	4.34
0709-8	No. 5 Floor	Sandstone	27.76	27.98	0.2	412	8.68	633	>5
0709-9		Sandstone	27.98	30.24	2.3	102	5.15	554	2.75
0709-10		Sandstone	30.24	32.94	2.7	28	2.01	360	0.25
0709-11		Sandstone	32.97	39.00	6.0	28	3.91	565	0.17
0709-12		Sandstone	39.00	44.74	5.7	20	2.65	1703	0.07
0709-13		Sandstone	44.74	47.31	2.6	20	5.12	1240	0.14
0709-14		Sandstone	47.29	50.11	2.8	43	6.42	648	1.27
0709-15	No. 4 Roof	Sandstone	50.11	50.84	0.8	131	8.06	957	>5
0709-16	No. 4 Floor	Mudstone/Coal	55.28	55.83	0.6	127	7.84	488	>5
QU-05-06A and QU-05-07									
05-6A/A/R1		Sandstone	16.71	17.6	0.89	103	6.95	721	4.94
05-6A/A/R2		Sandstone	13.635	16.61	2.975	80	5.48	712	3.73
07-7A/R1/R2/R3	Composite	Sandstone	44.51	47.05	2.54	77	4.45	381	2.97
Hole QU-08-22G									
1-5-09 A		Mudstone	15.20	15.24	0.04	10.2	1.47	32	1.31
1-5-09 B		Mudstone	15.24	15.45	0.21	39.8	5.6	120	4.34
1-5-09 C		Mudstone	15.45	16.05	0.60	16.8	7.96	300	5.42
1-5-09 D		Siltstone	16.05	16.85	0.80	9.1	7.77	483	4.4
1-5-09 E		Siltstone	16.85	18.33	1.48	7.9	9.1	963	1.14
1-5-09 F		Siltstone	18.33	20.09	1.76	7.2	8.85	1208	0.79
1-5-09 G		Siltstone	20.09	21.09	1.07	9.2	9.89	1481	0.96
1-5-09 H		Siltstone	21.09	22.14	1.05	14.7	6.93	475	2.47
1-5-09 I		Sandstone	22.14	23.97	1.83	10.9	5.54	668	1.11
1-5-09 J		Sandstone	23.97	25.26	1.29	7	5.97	1887	1.36
1-5-09 K		Siltstone	25.26	26.81	1.55	10.1	6.29	652	3.12
1-5-09 L		Siltstone	26.81	27.67	0.86	11.4	7.08	686	4.24
1-5-09 M		Siltstone	27.67	28.14	0.47	18.3	7.21	624	5.17

Table C-2 cont'd. Selected data from the 7 South strata (adapted from QCC, 2010)

Sample No.	Drill Hole	Description	Sample Composition	As [ppm]	Fe %	Mn [ppm]	S %
Coarse Reject Samples		<i>Average Crustal Abundance:</i>		1.8	5.65	950	0.035
Sample 1	QU-07-07	Coarse Reject	4-4L Comp	67.5	0.99	128	0.94
Sample 2	QU-07-09	Coarse Reject	4-4L Comp	43.6	2.1	180	1.68
81197	QU-08-03	Coarse Reject	4-4L Comp	188.3	4.2	189	4.94
81520	QU-08-05	Coarse Reject	4-4L Comp	27.8	1.55	139	1.82
81521	QU-08-07	Coarse Reject	4-4L Comp	135.8	2.73	175	2.74
81522	QU-08-08	Coarse Reject	4-4L Comp	192.7	3.16	154	3.32
80950	QU-08-04	Coarse Reject	4 (Main)	168	3.76	145	4.41
82417	QU-08-08	Coarse Reject	4L (Lower Plies Comp)	170.7	2.79	212	2.23
<b>Parting Samples</b>							
0707-02	Q/U-07-7	Ptg.	5L/4	243.7	7.36	134	8.45
80502	QU 08-5	Ptg.	5L/4	128.2	6.12	227	5.35
0707-04	Q/U-07-7	Ptg.	4/4L	42.3	0.30	25	0.11
0708-02	QU-07-8	Ptg.	4/4L	10.8	1.31	111	0.30
0709-03	QU-07-9	Ptg.	4/4L	4.8	0.89	202	0.06
80504	QU 08-5	Ptg.	4/4L	10.7	0.43	107	0.29
80702	QU 08-7	Ptg.	4/4L	12.1	1.00	164	0.29
81304	QU 08-13	Ptg.	4/4L	260.9	6.40	193	6.98
80803	QU 08-8	Ptg.	4/4L	56.2	1.20	222	0.26
80604	QU 08-6	Ptg.	4/4L	64.3	1.33	367	0.11
80903	QU 08-9	Ptg.	4/4L	11.8	0.45	95	0.17
81102	QU 08-11	Ptg.	4/4L	16.4	1.36	466	0.06
81202	QU 08-12	Ptg.	4/4L	85.2	3.47	409	2.78
<b>Raw Coal, Coarse Reject and Railings Samples</b>							
92050	QU-09-01	Raw Coal	Raw Coal	58.6	1.26	75	1.52
92051	QU-09-01	4 Upper	Coarse Reject + 100 mesh	92.2	3.25	163	3.56
92052	QU-09-01	4 Lower	Coarse Reject + 100 mesh	42	2.45	104	2.45
92053	QU-09-01	4 Upper & 4 Lower	Coarse Reject Saturated	59.7	2.79	148	2.9
92054	QU-09-01	4 Upper & 4 Lower	Coarse Reject Saturated	68.1	3.19	137	3.33
92055	QU-09-01	4 Upper & 4 Lower	Tailings Fines (-100 mesh)	86.1	1.73	224	1.69