ARSENIC SPECIATION AND THE CONTROLS ON ITS RELEASE IN CONTAMINATED SEDIMENTS AND CORRESPONDING TOXICOLOGICAL EFFECTS AT GIANT MINE, NWT

by

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Abstract

Arsenic (As) contamination presents an ecosystem and human health risk at Giant Mine, a historic gold mine near Yellowknife, NWT currently undergoing the final stages of assessment for remediation. Arsenic concentration is elevated in sediments at Giant Mine due to contamination from several forms of mine waste including flotation tailings, roaster calcine and impoundment spills. The Giant Mine Remediation Project has stated aims to remediate the surface of the site, including Baker Creek which runs through the property, to a condition that is a productive environmental habitat and spawning ground.

Environmental scanning electron microscope (ESEM) and synchrotron-based micro- X-ray Absorption Near Edge Spectroscopy (μXANES), micro-X-ray fluorescence (μXRF) and micro-X-ray diffraction (μXRD) techniques were employed to characterize the As-host phases and determine the solid-phase speciation of As in mine waste and sediments. Arsenopyrite, Fe-oxides, Fe-root plaque, and As_2O_3 were the major phases identified.

Sediment toxicity was measured using 10-day *Chironomus dilutes* and 21-day *Pimephales promelas* exposure tests. The toxicity tests found responses ranging of from 100% mortality at the most contaminated site to no statistical difference to the control groups in the least As contaminated site. Toxicity test chamber conditions were directly monitored with dialysis probes (mini-peepers) and Diffusive Gradients in Thin Films (DGTs).

DGT and mini-peeper deployment in the test beakers allowed for direct correlation of their measurements to trace metal uptake and bioaccumulation during the toxicity tests. Linear regression and ANOVA statistics were used to correlate, when possible, As tissue concentrations in *Chironomus dilutes* and *Pimephales promelas* to DGT, mini-peeper and surface water concentration measurements. Statistical analysis was also conducted for Co, Cr, Cu, Ni, Pb, Zn, and Sb though these other metal/metalloids were not always suitable for analysis due to constraints caused by detection limits.

It was found that DGT As was statistically correlated (r^2=0.836 and $p<0.0005$) to uptake in *Pimephales promelas* but that total element concentrations were also statistically relevant and slightly

better at predicting uptake (r^2=0.873 and $p<0.0005$). Mini-peepers could not be analyzed statistically due to challenges in their use within some highly vegetated sediment samples.

Co-Authorship

Chapter 3 of this thesis was prepared as a manuscript chapter in preparation for eventual publication as a co-authored paper. It was co-authored with Dr. H. Jamieson and Dr. P. Huntsman-Mapila who conceived the project and acted in supervisory positions. Dr. H. Jamieson and Dr. P. Huntsman-Mapila also participated in the field work, data collection and toxicity test maintenance.

Acknowledgements

Sir Isaac Newton is well remembered for saying

"If I have seen further it is by standing on the shoulders of giants"

but it less widely recalled that he was referencing his physically diminutive rival, Robert Hooke, and he was probably just being a jerk. Since the Queen's Geology Department has been a nurturing environment and I have no archrivals to insult I would like to appropriate Sir Newton's clever insult for sincere use. I have received the greatest of support from my many colleagues and I couldn't have done completed this degree without you all.

Foremost of all, I would like thank my supervisors Dr. Heather Jamieson and Dr. Philippa Huntsman-Mapilla. Without their guidance and vision this thesis would not have been possible. Special thanks is also owed to Carrie Rickwood for introducing me to the world of fish rearing and keeping me on the right path with regards to fish-statistics.

This project had a number of supporters, both financial and otherwise, who have my sincerest gratitude: Aboriginal Affairs and Northern Development Canada, Natural Resources Canada, Northern Scientific Training Program and Queen's University.

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List of Abbreviations

ANOVA	Analysis of Variance
(aq)	Aqueous
BPOND	Baker Pond
BVEG	Baker Creek Outlet Vegetated
DGTs	Diffusive Gradients in Thin Films
EEM	Environmental Effects Monitoring
ESEM	Environmental Scanning Electron Microscope
ESP	Electrostatic Precipitator
GSLW	Great Slave Lake Water
HPLC ICP-MS	High Performance Liquid Chromatography Inductively-Coupled Plasma Mass Spectrometry
ICP AES	Inductively Coupled Plasma Atomic Emission Spectrometry
LS	Lab Standard
NWT	Northwest Territories
RO	roaster oxide
RS	Research Standard
SWI	Sediment-Water Interface
µXANES	Micro-X-Ray Absorption Near Edge Structure
uXRD	Micro-X-Ray Diffraction
uXRF	Micro-X-Ray Fluorescence
YKB	Yellowknife Bay Beach

Chapter 1

Introduction

1.1 Giant Mine, Remediation Plan and Research Goals

Giant Mine, Yellowknife, N.W.T. is an abandoned mine site where processing and mining operations have produced contaminated surface and subsurface material such as As-contaminated sediments with a maximum of 21300 mg/kg As and an average of 1643 mg/kg As in Baker Creek which runs through the mine (Indian and Northern Affairs Canada, 2007).

During the mine's operation from 1948 to 2004 roughly 220,000kg of gold was produced. The gold was hosted in refractory arsenopyrite (FeAsS) ore which required roasting in order to make the ore susceptible to cyanidation (Coleman, 1957). The 237,000 tonnes of arsenic captured by the electrostatic precipitator (ESP) and baghouse were primarily stored in underground chambers. The mining process has caused the local permafrost to retreat. Much of the recent concern around Giant Mine stems from the arsenic's solubility in the absence of this permafrost. Installation of both active and passive heat transfer systems are now required to ensure long term stability through in-situ freezing (Indian and Northern Affairs Canada, 2007).

The Yellowknife area has been studied for the As in its environment, biota, and human health as early as 1949 (CPHA, 1977,Walker, 2006).The case of Giant Mine highlights a complex example of the redistribution of previously isolated natural As (as it was largely refractory) into more available environmental forms.

To address the complicated history and potential for further release to the environment the Giant Mine Remediation Plan is being finalized (at the time of writing). It has which has five stated aims which are to: (1) manage underground As_2O_3, (2) remediate the surface of the site to industrial and other more stringent guidelines, (3) manage risk to the public from mine buildings and openings, (4) minimize the

release of contaminants from the site the surrounding environment and (5) to restore Baker Creek to a condition that is a productive environmental habitat and spawning ground.

The primary research objective of this thesis is to investigate solid phase As hosts in impacted stream and lake sediments near Giant Mine, measure bioaccessible and labile As concentrations using multiple sampling techniques, and determine which methods best correlate with and predict element uptake. The research conducted in this thesis is relevant to the Baker Creek restoration plans contained in the Giant Mine Remediation Plan. Two of the three sites studied in this research lie within Baker Creek. To conduct this research the following steps were undertaken:

- Conducted detailed sampling and characterization of the co-existing sediment, pore-water and surface water, including aqueous and solid phase As speciation, at three selected sites.
- Examined the relationship, if any, between sequential extractions and pore-water concentrations.
- Measured sediment toxicity with using *Chironomus dilutes* and *Pimephales promelas* model organisms.
- Measured sediment labile and bioaccessible metal/metalloid concentrations using thin films (DGTs), mini-peepers (dialysis cells) and surface water concentrations.
- Used statistical analysis to rank DGTs, mini-peeper, and surface water concentrations on their capacity to predict toxicity and uptake in the model organisms.

1.2 Background

1.2.1 Geology and Processing at Giant Mine

Giant Mine is a historic gold mine located approximately 5 km north of the City of Yellowknife, NWT, Canada. It is one of two gold mines located close to Yellowknife, the other being Con Mine. The Giant Mine gold deposit occurs within the Archean Yellowknife Greenstone Belt which is bounded on the west by the Western Plutonic Complex and to the east by the Burwash Formation (Cousens *et al.*, 2002). Mineralization at Giant Mine occurs as disseminated sulfides and sulfosalts in broad silicified zones and quartz carbonate veins (Boyle, 1960). The gold is primarily refractory, being mostly hosted within

arsenopyrite that makes it unsusceptible to conventional cyanide extraction (Canam, 2006) though some free gold is present.

Milling of Giant Mine refractory gold ore involved crushing, grinding, and flotation to mechanically concentrate gold-bearing sulfides which was then roasted. Roasting occurred in an oxygen rich environment to breakdown the arsenopyrite ore and render the gold amenable to traditional cyanide extraction (Walker, 2006).

1.2.1.1 Aerial emissions

In the first three years of operation (1948-1951) roasting at Giant Mine released more than 7000 tonnes of As to the atmosphere and surrounding environment through stack emissions. Emission rates steadily improved over the life span of the mine with implementation of successive generations of capture and filtering technology. 1990s emissions rates were much lower at roughly 3-8 tonnes per year (Wrye, 2008). A study of deposition rates in the 1970s determined that local As deposition rate were roughly 55 kg per square mile per year (CPHA, 1977; Walker, 2006).

Roasting was conducted to convert arsenopyrite containing refractory gold to porous Fe-oxides in order to make the gold amenable to traditional cyanide leaching methods of extraction (Jamieson, 2011). The roaster-derived Fe-oxides left after roasting have been documented containing up to 7wt% As in nanocrystalline structures composed of composites of maghemite, hematite, and magnetite. Due to their formation during an oxidation process (roasting) they can contain both As (III) and As (V) states (Walker *et al.*, 2005).

$$2FeAsS + 5O_2 \rightarrow Fe_2O_3 + As_2O_3 + 2SO_2$$

Researchers have directly observed a product of the roasting process, As_2O_3, in Giant Mine soils using scanning electron microscopy and micro X-ray diffraction (Wrye, 2008; Bromstad, 2011). Even after redistribution through solubilization, volatization, and wind and water transport current arsenic content in soils in still primarily influenced by early As emissions from 1949 to 1964 before the most

significant environmental controls were placed on stack emissions. The aerially distributed As is primarily in the form of a As_2O_3 particulate (Bromstad, 2011).

Studies of other As_2O_3-impacted sites have shown that in many cases the mineral does not persist for decades as it has at Giant Mine. Yang and Donahoe (2007) examined two industrial sites contaminated with As_2O_3 herbicide in the 1950s and 1960s and found that it was no longer present, having dissolved and partially adsorbed onto other species.

Several factors are thought to contribute to why the Giant Mine As_2O_3 is less soluble than at other sites. First, Giant Mine As is immobilized for over half the year while the ground is frozen. Additionally, trace antimony (Sb) content, an inherent property of the As_2O_3-rich dust at Giant greatly influences solubility. Solubility testing of low-Sb As_2O_3 shows that it preferentially dissolves compared to high-Sb As_2O_3 at temperatures below 100°C. It is hypothesized that Sb within As_2O_3 can lower As_2O_3 solubility by reducing the thermodynamic activity of As_2O_3 (Riveros *et al.* 2000).

1.2.1.2 Tailings Streams

During the first three years of mine operation (1948-1951) tailings were deposited on the shore of Yellowknife Bay without further treatment. After 1951 tailings were discharged into a lake on the mine site and other low-lying areas. Dams were first constructed in the 1950s to increase tailings storage capacity. In the 1970s “clay core” dams were constructed to contain new tailings (Indian and Northern Affairs Canada, 2007).

The tailings produced at Giant Mine can be split into three separate streams of distinct chemical and physical properties that contain the bulk of the As contaminating the surface of the mine. These include floatation tailings, cyanided calcine residue and roaster dust/precipitate. Floatation tailings are high tonnage and low As, which is primarily present in arsenopyrite. Calcine (As hosted in iron-oxides) and roaster dust (As hosted in arsenic trioxide) are lower tonnage but have higher As concentrations as roasted products of the sulfide concentrate (Walker 2006). Roaster dust was deposited aerially in the surrounding environment and captured by baghouse and precipitator technology. Changes within these

streams occurred over time as milling, processing, and precipitator technology and practices advanced (Table 1-1).

Tailings Stream	Year	Discharge rate (tonnes per day)	As Concentration (% wt.)
Flotation	1999	1000	0.09
	1963	794	0.28
Calcine Residue	1999	170	1.8
	1963	122	1.2
ESP Residue	1999	9	4.4
	1963	9	6.2

Table 1-1: Arsenic concentration in the waste tailings streams produced during mining. Changing technology and practices altered the As discharge rate and loading in these tailings. Modified from Walker 2006.

1.2.1.3 Arsenic Sediment Contamination

Ranging from Reach 0 (Baker Outlet) to Reach 6 (Baker Pond), Baker Creek is delineated into seven sections along its length in the Remediation Plan and the supporting documents (Golder Associates, 2013).

Baker Pond currently receives treated effluent from the mine on a seasonal basis. The bottom of Baker Pond and the shoreline contain mine tailings which were disturbed in May 2011 as a result of the change in flow caused by ice accumulation. A large marsh area is located at the mouth of Baker Creek where it flows into Yellowknife Bay behind a constructed breakwater.

Previous research has suggested that historic sediment As contamination in Baker Creek and Yellowknife Bay pose much greater risk to aquatic life than the seasonal discharge of mine effluent to these environments (Dillon Consulting, 2002; SENES Consulting, 2006).

1.2.1.4 Effluent

Dewatering operations within the mine are necessary to prevent flooding. Water enters the mine from groundwater, infiltration through soils and bedrock in the mine area, runoff flowing into the open pits, seepage from Baker Creek, and seepage from the tailings containment areas (INAC 2007). Prior to 1981 this mine influent was pumped directly into Baker Creek. An effluent treatment plant was installed

in 1981 was installed to oxidize As(III) to As(V) and precipitate the As with addition of ferric sulphate with an iron to arsenic molar ratio of 10:1 is established. After treatment, effluent was released to a settling pond, followed by a polishing pond, and finally discharge into Baker Pond.

During the summer months the water is treated and discharged into Baker Creek. The arsenic concentration in the North and Northwest ponds, where water is stored before treatment and discharge to Baker Creek is typically between 7 and 20 mg/L. Giant Mines water license limits the maximum allowable arsenic concentration in the discharge to 0.5 mg/L (INAC 2007) which is in compliance with the Metal Mining Effluent Regulations (0.5 mg/L) (Government of Canada, 2012) but above the water quality guideline for the protection of freshwater aquatic life (0.005 mg/L) (CCME 2001). Treated effluent is currently the main source of As to the Baker Creek receiving environment (Golder Associates, 2013).

1.2.1.5 Arsenic Sediment Guidelines

The Canadian Council of Ministers for the Environment (CCME) sets guidelines for arsenic concentration in water, sediments, and soils for protection of humans, other organisms, and the environment. The CCME interim sediment quality guideline for the protection of aquatic life in freshwater systems is 5.9 ppm (Canadian Council of Ministers of the Environment, 1999). Yellowknife has site specific guidelines higher than the national average due to naturally high concentrations and reduced opportunities for exposure due to an extended winter season (Table 1-2).

Medium	**Land Use**		
	Residential	**Industrial**	**Boat Launch**
Soil	160	340	220
Sediment	N/A	N/A	150

Table 1-2: The site specific concentration guidelines for arsenic concentration in soil and sediments (in mg/kg) near Giant Mine and Yellowknife, NWT (GNWT 2003) for protection of human health.

Medium	Soil Land Use				Sediment Environment	
	Agricultural	**Residential**	**Commercial**	**Industrial**	**Freshwater**	**Marine**
Soil	12	12	12	12	5.9	7.24

Table 1-3: The national concentration guidelines for soil bearing arsenic in Canada (in mg/kg) for the protection of environmental and human health (CCME 2001b) and the national interim concentration guidelines for sediments (in mg/kg) for the protection of aquatic life (CCME 2001).

1.2.1.6 Historic Arsenic in Sediments

Baker Creek runs through the Giant Mine property before discharging into Yellowknife Bay. It is known to have significant As contamination with the majority of fish and benthic organisms disappearing from the habitat during peak mining. One of the remediation plan objectives is to "restore Baker Creek to a condition that is as productive as possible, given the constraints of hydrology and climate" (Golder Associates, 2013). Two of the three sites studied in this report lie on Baker Creek.

There are four sources of arsenic contamination relevant to sediments in the Baker Creek. They are: historic deposition of arsenic trioxide from the air (Wrye 2008; Bromstad 2011), leachate from fill used in the construction of structures (Golder Associates, 2005), occasional tailings spills, and the decanting of historic untreated water prior to 1981 that took place every spring in the tailings ponds (Andrade et. al. 2010; SRK 1998; INAC 2007).

Baker Outlet is one of the most highly studied areas on Baker Creek. The area has attracted interest for being publicly accessible, the point of deposition for the silt carried by Baker Creek, and the subsequent marsh habitat that was established by the sedimentation.

The Baker Creek Outlet sediment sampling record is well defined spatially.

Figure 1-1 shows the sampling locations for several previous researchers. Table 1-4 illustrates the extreme variation in sediment As concentration in adjacent sampling sites. Because the method of sampling varied between surficial grab samples (estimated to be 5cm deep) and vertical coring both the bulk average arsenic concentration for the first 5cm of sediment and the range of concentrations in sediment cores are presented to allow for comparison.

As can be seen in Table 1-4 the sediments in the Baker Creek Outlet greatly exceed the guidelines of Table 1-2. Because these sediments have no official use (though a boat club is located nearby) human exposure is fairly limited when the area is only used as a boat launch.

Arsenic concentrations were found by Golder (2008) to be most variable within Baker Outlet and Reach 2 where peak concentrations were more than an order of magnitude higher that those measured at other stations within the same reach.

Site	Avg As 1-5cm (mg/kg)	Core Range (mg/kg)	Core Depth (cm)	Source
Baker Creek Channel				
C1	1825	206-2197	15	Mace 1998
C2	359	26.3-580.4	22	Fawcett 2009
C3	2550	N/A	~5	Jackson1996 via Mace 1998
C4	1296	115.9-5406.3	18.5	Andrade 2006
Baker Creek Vegetated				
V1	278	N/A	~5	Mace
V2	2133.8	93-3699.6	44	Fawcett 2009
V3	2661	N/A	20	Stephen 2011

Table 1-4: Arsenic concentrations in the Baker Creek outlet sediments. See Figure 5 for locations. Significant figures are those indicated by authors.

Figure 1-1: The Baker Creek outlet area sampling locations Modified from Google Maps, 2012. See Table 1-4 for As concentrations.

All samples that were measured as vertical profiles showed at least some degree of mid-core enrichment at 5-15 cm below the SWI. Radiometric dating of the lacustrine sediments in Yellowknife Bay has been used to confirm that the enrichment seen within Yellowknife Bay corresponds to the beginning of Giant Mine activity (Andrade et al., 2011). The peak of the mid-core enrichment occurs during increased production at the mine and minimal environmental controls.

1.2.1.7 Historic Arsenic in Sediments Construction and Disturbances

In 2007 a major construction initiative took place in order to reroute a section of Baker Creek away from the C1 pit (SRK 2007). It was observed in 2005 and 2006 that previously minimal infiltration rates into the C1 pit (see Figure 1) from Baker Creek were increasing. The C1 pit drains directly into the mine because the bottom of the pit intersects with several backfilled stopes. To prevent further flooding a

section of Baker Creek in Reach 4 was rerouted away from the pit. Additionally, a bituminous geomembrane liner was installed in the southern 170 m of the new channel (SRK 2007). Preliminary data collected in 2004 (Golder Associates, 2013) suggest that benthic invertebrates had recolonized Baker Creek in Reach 4 prior to the reroute.

Mine waste discharged into Baker Creek has accumulated at its outlet into Yellowknife Bay throughout the life of the mine. However, this sediment has accumulated more rapidly after the addition of the breakwater in 1964 (Fawcett, 2009). The sediment is preferentially trapped in the Baker Creek Vegetated (BCV) area. Prior to 1981, this sediment and the water that carried it had much higher arsenic content due to lack of emission controls, such as pre-treatment of mine water before discharge into the creek (INAC 2007). The arsenic content of these sediments is not likely to increase in the future, providing no major releases of arsenic occur at the mine. Treatment of water emitted from the mine will ensure that the water in Baker Creek is lower than it was historically. With the end of mining and roasting the four inputs of arsenic are either removed or greatly diminished. However, the arsenic in the sediments may or may not remain over the long term.

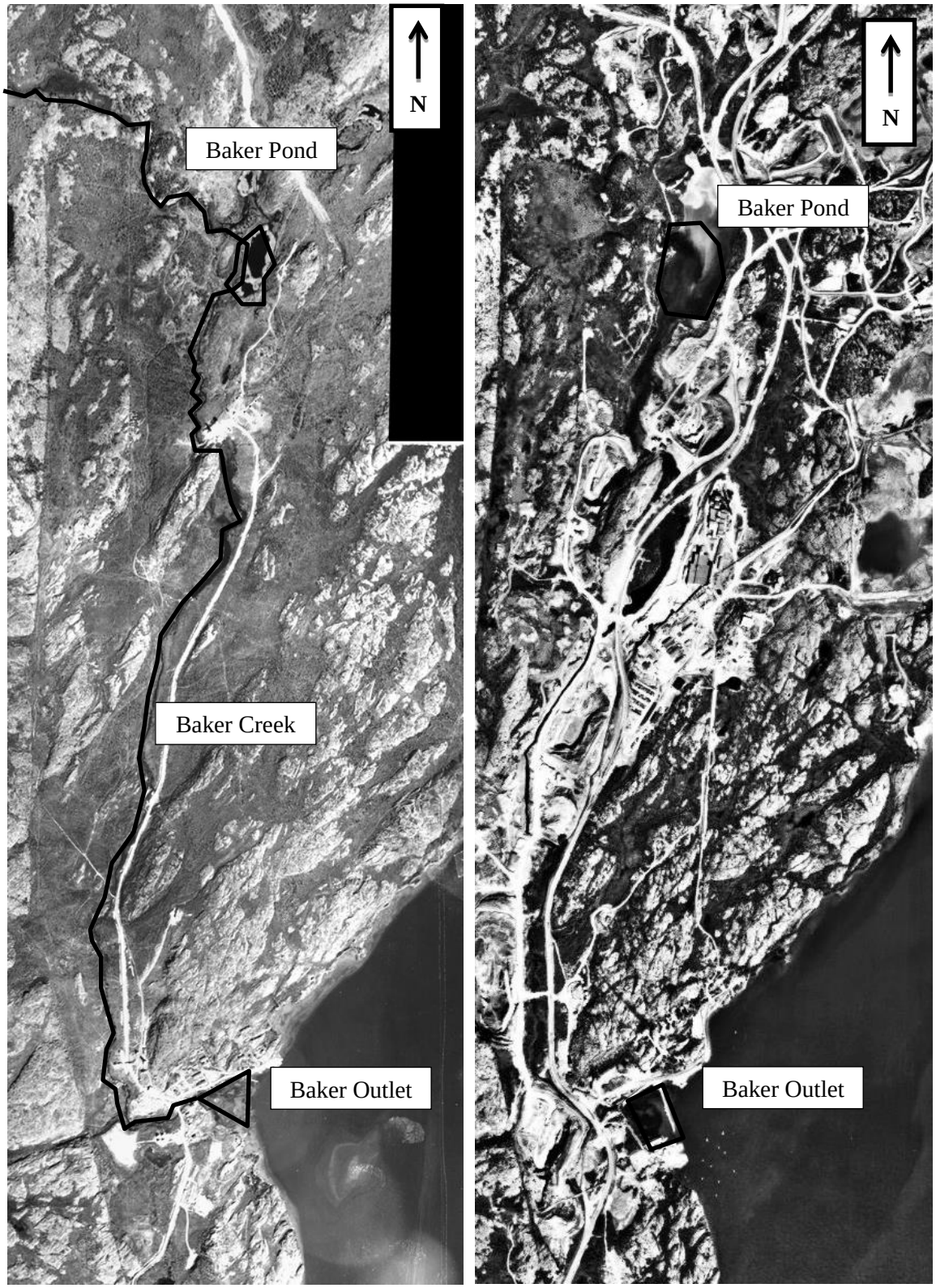


Figure 1-2: A series of air photos of Giant Mine from 1946 (left) and 1988 (right). Note the expansion of Baker Pond and the breakwater built at Baker Outlet. Photos were digitally stitched together using Microsoft Research Photo Stich software.

1.3 Previous Work in Biological Sampling

1.3.1 Benthic Invertebrate

The Yellowknife River was a control site in the Giant Mine Remediation Plan and considered unaffected by the mining process. Information on the benthic invertebrate community within the Yellowknife River is somewhat limited (Golder 2008a) as it is less thoroughly studied than Baker Creek. Falk et al. (1973) sampled the river in 1972 and found 25 genera. The benthic invertebrate community was dominated by chironomids, oligochaetes and nematodes. Additionally, biting midges, clams, and snails were also relatively abundant in the Yellowknife River.

Benthic invertebrate populations were mostly absent downstream of Giant Mine effluent release in historical studies of the 1970s. This absence of communities was attributed to elevated As concentrations (Falk *et al.*, 1973,Golder Associates, 2013). Another historic study found only one benthic invertebrate present in lower Baker Creek where oligochaetes (aquatic worms) were observed in low numbers at less than 100 individuals per square meter (Moore, 1978;Golder Associates, 2013).

In July 2002 a sampling study observed dipteran (true fly), Ephemeroptera (mayfly), Plecoptera (stonefly), and Trichoptera (caddishfly) larvae in Baker Creek at location upstream of the mine with Dipteran larvae being the most abundant. Ephemeroptera, Plecoptera, and Trichoptera were absent from locations downstream of the mine (higher As concentrations due to effluent) but oligochaetes, ostracods and dipteran larvae were present. The absence of Ephemeroptera, Plecoptera, and Trichoptera taxa have been used as an indicator of toxicity in aquatic systems previously (Dillon Consulting, 2002).

A more recent (Golder Associates, 2006) quantitative benthic invertebrate study conducted in Baker Creek as part of the Phase 1 and 2 EEM programs evaluated the toxicity of the treated periodic effluent discharge into Baker Creek. Artificial substrate samplers were deployed close to the mouth of Baker Creek and in a reference area for a colonizing period of 66-70 days. The artificial substrates were located on the stream bed where colonizing invertebrates were primarily exposed to waterborne contaminants. Both studies concluded that effects of the present day effluent discharge on the benthic

convertibrate community could be characterized as low. Historical sediment contamination likely poses a greater risk to aquatic life in Yellowknife Bay (Golder Associates, 2006).

1.3.2 Fish communities

Reach 4 of the creek was realigned in summer 2006 and lacks historical sediment contamination. Since the realignment, spawning by Arctic Grayling, Northern Pike and Sucker species has been observed. A number of recent fish surveys have documented fish species, including arctic grayling, walleye and northern pike residing and spawning in the lower areas of Baker Creek during the spring spawning period, but they do not persist upstream (Golder Associates, 2012).

A fish salvage in a pond (downstream of effluent discharge) on Baker Creek was conducted in winter 2006 when Baker Creek was being rerouted away from the Mill area (Golder 2008). A total of 93 fish were removed from the pond. Six different species of fish of various ages and sizes were captured: Northern Pike, Burbot, Lake Whitefish, Longnose Sucker, Ninespine Stickleback and Lake Cisco (Indian and Northern Affairs Canada, 2007) indicating significant return of fish to Baker Creek.

1.4 Thesis Layout

Chapter 1 has introduced the history of mining and contamination at Giant Mine within the context of the Giant Mine Remediation Plan and the Baker Creek Assessment projects. Chapter 2 is a literature review of relevant As hosts at Giant Mine and the controls on their mobility and aqueous speciation. Chapter 3 is a manuscript prepared for future publication in a journal. Chapter 4 contains the conclusions of the thesis and suggestions for future work.

Chapter 2

Literature Review

2.1 Arsenic in the environment

2.1.1 Sources of Arsenic

Arsenic (As) is the twentieth most abundant element in the earth's crust. There are $2.5x10^{16}$kg of As in global sediments, $1.0x10^{12}$kg in global soil and $3.7x10^{12}$kg dissolved in the ocean (Mackenzie *et al.*, 1979).

Natural processes such as weathering, volcanic activity, and biological activity can mobilize arsenic from sequestration. Every year 17,150 tonnes of As are emitted to the atmosphere by volcanoes, 27 tonnes by the oceans, and 2,000 tonnes by naturally occurring forest fires (Matschullat, 2000).

Anthropogenic sources of As include: combustion of oil and coal by power plants, waste incineration, cement manufacturing, animal farming waste, glassware production, electronics industries, ore processing, wood preservatives, pesticides, and pyrotechnics (Matschullat, 2000). It has been estimated that anthropogenic sources of atmospheric As amount to 70% of the global atmospheric As flux (Nriagu & Pacyna, 1988;Walker, 2006).

2.1.2 Arsenic in mining impacted sediments

Mining processes can produce wastes with As concentration up to weight percentages in the solid phase. Procedures for creating stable As-associated minerals for long term storage of concentrated As waste have been developed. Co-precipitation with iron, treatment with lime, and solidification within cement have all been used to sequester waste arsenic, with varying degrees of success. Significant attention has been paid to the precipitation of ferric arsenate (Palfy *et al.*, 1999; Opio, 2013). Unfortunately, processing and treatment practices of historic mines rarely achieved modern standards of environmental protection and stewardship.

Three waste streams with distinct chemical and physical properties compose the bulk of the tailings and contain the bulk of the As that has contaminated the surface of Giant Mine. These include flotation tailings, cyanided calcine residue and roaster dust/precipitate. Flotation tailings are high tonnage and low As, which is primarily present in arsenopyrite. Calcine (As hosted in iron-oxides) and roaster dust (As hosted in arsenic trioxide) are lower tonnage but have higher As concentrations as roasted products of the sulfide concentrate (Walker, 2006).

Elevated As concentrations can be found where mining has released a solid, liquid or gas into the environment. When in an aquatic setting the As is subject to the ambient conditions (pH, organic carbon, eH, evaporation, mixing, etc.) that will define whether the location becomes a sink or source for the As. Elevated arsenic concentrations can be found in both acidic mine drainage as well as circum-neutral environments (Majzlan *et al.*, 2011).

Mining-related ore roasting of arsenopyrite produces As2O3 and As-bearing roaster Fe oxides, as illustrated by the equation below (Bromstad, 2011):

$$2FeAsS + 5O_2 \rightarrow Fe_2O_3 + As_2O_3 + 2SO_2$$

Roasting is designed to convert arsenopyrite containing refractory gold to porous Fe-oxides in order to make the gold amenable to traditional cyanide leaching methods of extraction (Jamieson, 2011). Roaster-derived Fe-oxides (ROs) have been documented containing up to 7wt% As in nanocrystalline structures composed of composites of maghemite, hematite, and magnetite. Due to their formation during an oxidation process (roasting) they can contain both As (III) and As (V) states (Walker *et al.*, 2005).

Researchers have directly observed As_2O_3 in Giant Mine soils using scanning electron microscopy and micro X-ray diffraction (Bromstad , 2011; Wrye, 2008). Studies of other As_2O_3-impacted sites have shown in many cases that the mineral does not persist for decades as it has at Giant Mine. Yang and Donahoe (2007) examined two industrial sites contaminated with As_2O_3 herbicide in the 1950s and 60s and found that it was no longer present, having dissolved and partially adsorbed onto other species. However, near surface concentrations of total arsenic in outcrop soils at Giant Mine have been observed

to range from 156mg/kg to 5760mg/kg with an average of 1546mg/kg, which is higher than the tailings used as backfill in the mine (Bromstad, 2011). Most of this arsenic is in the form of arsenic trioxide.

Several factors are known to contribute to why the Giant Mine As_2O_3 is less soluble than at other sites. Giant Mine As is immobilized for over half the year while the ground is frozen and trace antimony content, an inherent property of the As_2O_3-rich dust at Giant greatly influences solubility. Solubility testing of low-Sb As_2O_3 dissolved preferentially compared to high-Sb As_2O_3 at temperatures below 100°C. It was hypothesized that Sb within As_2O_3 can lower As_2O_3 solubility by reducing the thermodynamic activity of As_2O_3 (Riveros *et al.*, 2000).

2.1.3 Speciation

Arsenic is a metalloid, with intermediate properties between a metal and non-metal. Arsenic is redox sensitive and is chalcophilic (bonds preferentially to sulphur over oxygen). The most ubiquitous arsenic bearing mineral is arsenopyrite (FeAsS) (Reimann *et al.*, 2009). There are more than 300 additional naturally occurring arsenic minerals. Of these other mineral approximately 60% are arsenates, 20% are sulphides and sulphosalts, 10% are oxides while the rest are arsenites, arsenides, native elements and metal alloys (Drahota & Filippi, 2009).

Arsenic can also be found in organic compounds when biological activity of the arsenic is present and where dissolved organic concentrations are exceedingly high (Smedley & Kinniburgh, 2002). Table 2-1 lists many of the common organoarsenicals that are found in natural systems.

Name	Abbreviation	Chemical Formula
Monomethylarsonic acid	MMA^{V}	$CH_3AsO(OH)_2$
Monomethylarsonous acid	MMA^{III}	$CH_3As(OH)_2$
Dimethylarsinic acid	DMA^{V}	$(CH_3)_2AsO(OH)$
Dimethylarsinous acid	DMA^{III}	$(CH_3)_2AsOH$
Dimethylarsinoyl ethanol	DMAE	$(CH_3)_2AsOCH_2CH_2OH$
Trimethylarsine oxide	TMAO	$(CH_3)_3AsO$
Tetramethylarsonium ion	Me_4As^+	$(CH_3)_4As^+$
Arsenobetaine	AsB	$(CH_3)_3As^+CH_2$
Arsenobetaine 2	AsB-2	$(CH_3)_3As^+CH_2CH_2COO^-$
Arsenocholine	AsC	$(CH_3)_3As^+CH_2CH_2OH$
Trimethylarsine	TMA^{III}	$(CH_3)_3As$

Table 2-1: A list of common naturally occurring organoarsenicals and their abbreviations (modified from (Gong *et al.*, 2002)).

Many of the above compounds are methylation products of inorganic arsenic in humans and other organisms (MMA^{V}, MMA^{III}, DMA^{III}). In contrast to inorganic As, arsenobetaine is the primary form of arsenic in fish and is comparatively non-toxic to humans (Larsen *et al.*, 1993).

2.1.3.1 Redox

Arsenic is a redox-sensitive element. Inorganic arsenic exists in multiple oxidation states as arsenate (+V), arsenite (+III), native arsenic (0), arsenic suphides (-I), and arsine (–III) (Bissen & Frimmel, 2003; Bromstad, 2011). Arsenate (AsO_4^{-3}) and arsenite (AsO_3^{-3}) are the predominant forms of arsenic in natural ground water.

Redox potential and pH are the main controls of As speciation in natural waters. Arsanate and arsenite are oxyanions each with three levels of protonation controlled by pH and eH. Figure 2-1 illustrates oxidation state and protonation as a function of eH and pH and the equation below is the balanced chemical equation governing the oxidation of As(III). Many lake and stream sediments are near-neutral and thus dominated $H_3AsO_3^0$, $H_2AsO_4^-$, and $HAsO_4^{-2}$. Arsenate generally predominates under oxidizing conditions though oxidation state and speciation are rarely in equilibrium. Kinetics are known to have a significant effect on ratios of arsenate to arsenite in natural waters; it is common As(V):As(III) ratios to be lower than expected in oxidizing water conditions (Smedley & Kinniburgh, 2002).

$$H_3AsO^0_{3(aq)} + \frac{1}{2}\,O_{2(g)} \rightarrow H_2AsO^-_{4(aq)} + H^+_{(aq)}$$

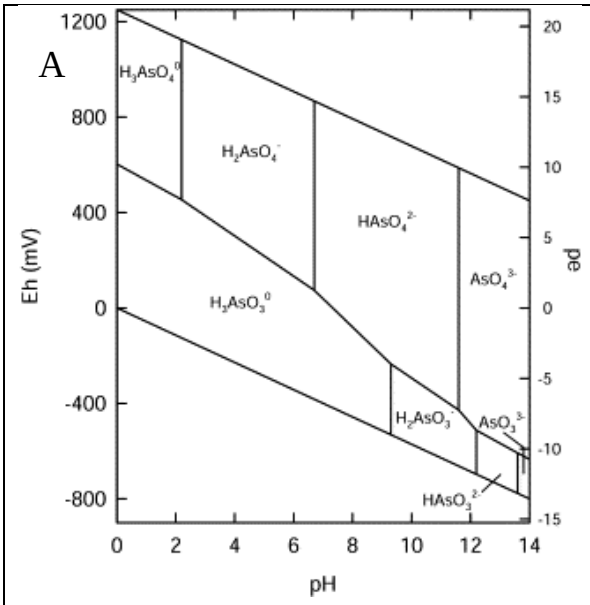


Figure 2-1-A. Eh-pH diagram for inorganic aqueous As in the As-O_2-H_2O system at 25°C and 1 bar pressure.

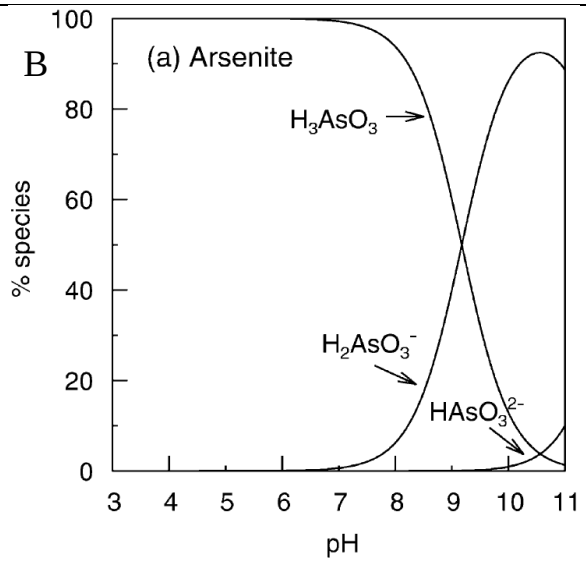


Figure 2-1-B. Arsenite speciation as a function of pH (ionic strength of about 0.01M). Redox conditions have so that As(III) is dominant.

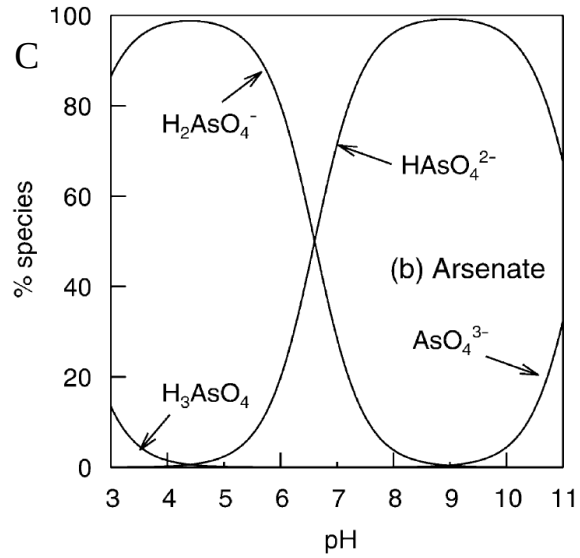


Figure 2-1-C. Arsenate speciation as a function of pH (ionic strength of about 0.01M). Redox conditions have been chosen so that As(V) is dominant (McCleskey *et al.*, 2004)

The kinetics of As(III) oxidation and As(V) reduction are slow. In the absence of other oxidants or reductants As(V)/As(III) ratios can persist for weeks (McCleskey *et al.*, 2004). As(III) oxidation is inhibited unless metal catalysts , strong oxidants such as Fe(III), or light are present (Hug *et al.*, 2001) to catalyze the reaction. Microbial As(V) reduction can occur through two different processes: anaerobic respiration and detoxification. Many microorganisms are capable of using As (V) as a terminal electron acceptor for anaerobic respiration (McCleskey *et al.*, 2004)

2.1.2.2 Adsorption

Adsorption is an important mechanism for As attenuation in sediments, and desorption is an important As source. There are two broad categories of adsorption that govern the strength and reversibility of adsorption. Chemisorption occurs when strong inner-sphere surface complexation bonds form and physisorption occurs when weak electrostatic outer sphere complexation bonds form (Vaishya & Gupta, 2005).

Under neutral pH in oxic conditions, As can be effectively attenuated by adsorption with Fe, Mn, and Al oxides for remediation purposes (De Vitre *et al.*, 1991). Sorption of As decreases with the presence of other dissolved anions, such as bicarbonate and phosphate, that compete for sorption sites (Bauer & Blodau, 2006). In acidic soils As can also sorb to clay minerals and biogenic particles (Sadiq, 1997).

Arsenic adsorption onto Fe-oxides is pH dependent. As(V) adsorbs more strongly than As(III) at neutral pH. The point of zero charge (PZC) for Fe-oxides is roughly pH 8, below which the surface of the mineral is positively charged (Parks & Bruyn, 1962). The negatively charged As(V) ions $H_2AsO_4^-$, and $HAsO_4^{-2}$ that dominate at circum-neutral pH thus experience a stronger attraction to the Fe-oxide than the neutral As(III) species.

2.1.2.3 Humic Acid Complexes

Organic matter is ubiquitous in aquatic systems and affects the environmental behavior of As in a variety of ways. Microbial degradation of organics can lead to reductive dissolution of As coated Fe-oxides (McArthur *et al.*, 2001) by providing thermodynamically favorable oxidation products. Dissolved organic material also competes with As for binding onto adsorbents surfaces such as alumina, goethite, or hematite (Bauer & Blodau, 2006). Finally, complexation by humic acids can bind As and reduce bioavailability to aquatic organisms (Kalis *et al.*, 2006). Despite the known impact of organic matter on As speciation and mobility, data on the binding behavior of As(III) and As(V) with humic acids is less available compared to other elements (Buschmann *et al.*, 2006).

At neutral pH As(III) exists as a neutral complex, H_3AsO_3 while As(V) is present as the anions $HAsO_4^{-2}$ and $H_2AsO_4^-$ (Figure 2-1). In a study using commercially available humic acids As(V) was found to be more strongly bound than As(III) at all pHs. For As(III) and As(V), maximum binding at pH 7 was observed (Buschmann *et al.*, 2006).

In natural aquatic systems, cations such as Ca, Mg, and Fe are abundant. When interacting with organic ligands these cationic metals can act as both competitors and as promoters (via cation bridging) for the binding of the As with humic acid (Redman *et al.*, 2002). Binding mechanisms for As(V) and As(III) are suspected to be different, even when binding to the same functional group.

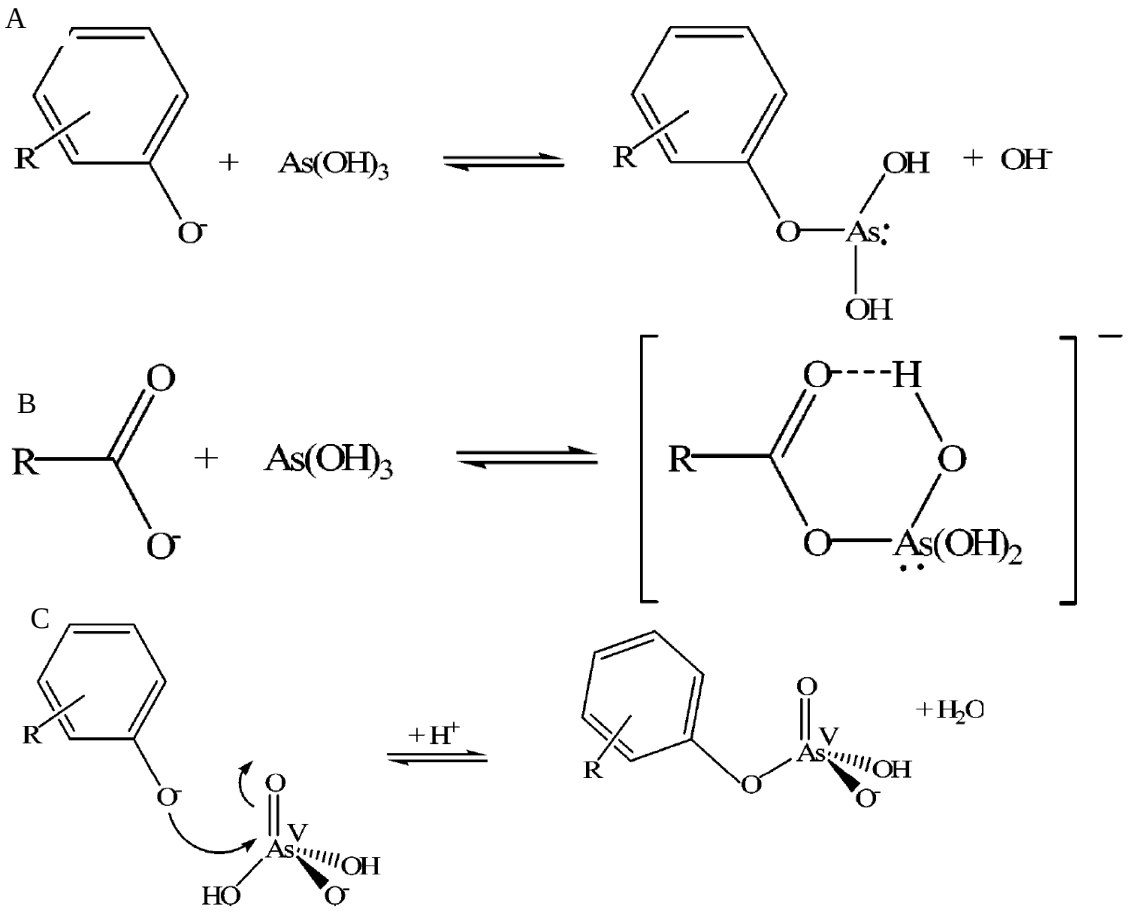


Figure 2-2: Proposed binding mechamisms for humic acid and As in aquoues systems. A: Humic acid bonding As(III) via a phenolate functional group to As(III) through π-bonding B: Humic acid bonding As(III) via a proposed reaction mechanism of a carboxylic group by forming a negatively charged adduct with stabilizing H-bridges C: Proposed model for humic acid bonding As(V) via as the arsenate center followed by protonation and water release (Buschmann *et al.*, 2006).

Arsenic complexes with hard inorganic ligands such as chloride and carbonate are weak compared to complexes with soft ligands such as sulfides and phenols (Spycher & Reed, 1989). Direct comparison of distribution coefficients in not yet possible for many As-binding organic studies because it has not been fully determined whether the As is bound by monodentate, bidentate, H-bridges, and/or van der Waals associations or what combination therein.

2.1.4 Uptake by vegetation

Arsenic is an element that is nonessential for and toxic to plants. It has been used as a pesticide, herbicide and fungicide (Garbarino *et al.*, 2003,Smedley & Kinniburgh, 2002). As(V) is taken up by phosphate transporters and some nodulin-like intrinsic proteins (NIPs) are able to transport As(III). In rice

(*Oryza sativa*), arsenite uptake also shares the silicon pathway of entry to root allowing for greater arsenic accumulation (Ma *et al.*, 2008) that is observed in rice paddies. In root cells arsenate is reduced to arsenite, and then transported to an external medium, complexed by thiol peptides or translocated to shoots (Zhao *et al.*, 2009).

Arsenic hyperaccumulation is found in select species of fern. The physiological processes that cause hyperaccumulation are not fully understood yet. Hyper tolerance is found in all natural hyperacumulators (Zhao *et al.*, 2009). The majority of As in hyperaccumulator species is inorganic arsenic stored in vacuoles (Zhao *et al.*, 2009; Wang *et al.*, 2002)

Typha latfolia (cattail) sequesters arsenic within predominantly Fe-oxide root coatings that decrease mobility within wetland sediments. Catail root plaque has been observed to adsorb (but not coprecipitate) arsenic in a ratio of 20% As(III) and 80% As(V) heterogeneously mixed throughout the plaque at a total concentration of up to 1% As (Blute *et al.*, 2004). *Typha dominguensis* (southern cattail) and *Schoenoplectus maritimus* (bayonet grass) has also been observed to have a root plaque arsenic concentration of up to 1% (Taggart *et al.*, 2009). It is possible that reductive dissolution of arsenic can occur in the wetland environment during vegetation loss.

Wetland plants can oxidize the immediate environment within tens to hundreds of microns of the roots. Some wetland macrophytes such as *Typha latifolia* (cattail) also develop porous tissue that enhances oxygen transport to the roots for respiration (Kludze & DeLaune, 1996). Sediment oxygenation may also protect wetland plants from the toxicity of reduced organic compounds via the mechanism of oxidized iron root plaque formation (Blute *et al.*, 2004). The primary Fe root-plaque phase is Fe(III) oxyhydroxide, goethite, and lepidocrocite (Taylor *et al.*, 1984).

The total amount of As sequestered in root plaque can be significant relative to the mass of dissolved As in the root zone of wetlands. Blute *et. al.* (2004) found that instantaneous release of all adsorbed arsenic in cattail root plaque would raise the As in the porewater 50 times higher than ambient porewater in the studied wetland in the absence of possible As redistribution into other solid phases. The concentration of As in root plaque was measured at 260-1200 µg/g wet plaque.

2.1.5 Arsenic Hosts Giant Mine Wastes

The tailings produced at Giant Mine can be split into three separate streams of distinct chemical and physical properties that contain the bulk of the As contaminating the surface of the mine. These include flotation tailings, cyanided calcine residue and roaster dust/precipitate. Flotation tailings are high tonnage and low As, which is primarily present in arsenopyrite. Calcine (As hosted in iron-oxides) and roaster dust (As hosted in arsenic trioxide) are lower tonnage but have higher As concentrations as roasted products of the sulfide concentrate (Walker 2006). Roaster dust was deposited aerially in the surrounding environment and captured by baghouse and precipitator technology. Changes within these streams occurred over time as milling, processing, and precipitator technology and practises advanced (Table 1-1).

Tailings Stream	Year	Discharge rate (tonnes per day)	As Concentration (% wt.)
Flotation	1999	1000	0.09
	1963	794	0.28
Calcine Residue	1999	170	1.8
	1963	122	1.2
ESP Residue	1999	9	4.4
	1963	9	6.2

Table 2-2: Arsenic concentration in the waste tailings streams produced during mining. Changing technology and practices altered the As discharge rate and loading in these tailings. Modified from Walker 2006.

Arsenic phases of As present in the calcine and ESP residue has been thoroughly investigated using linear combination fitting analysis of the XANES region. XANES analysis shows that As in roaster calcine and ESP residue is present three phases: As(V) bound to oxygen (As(V)-O), As(III) bound to oxygen (As(III)-O), and arsenopyrite (As(-I)-S). The XANES region can determine the As oxidation state and next nearest atom (based on shape with model compounds) but the exact mineral phase cannot be resolved through this method alone (Fawcett, 2009).

The roasting of gold ore at Giant Mine is a thermal oxidation process that decomposes sulfide minerals such as pyrite and arsenopyrite into porous Fe oxides including hematite, maghemite, or

magnetite. Roaster generated Fe-oxides are a primary anthropogenic As-bearing solid with high As content. The roasting of pyrite and arsenopyrite produces Fe-oxides with concentric or porous "spongy" texture depending on formation conditions and whether a pyrrhotite intermediate phase occurs (Walker, 2006).

The main As-bearing phase identified in Giant Mine calcine residues are nanocrystaline grains of maghemite containing <0.5 to 7% As (w/w) with a highly variable mixture of As(III)/As(V). Some maghemite grains were observed to have enriched As concentration on the edge believed to be deposited by As vapor in the roaster. Though As(III) is considered more mobile than As(V) and can be oxidised in the oxic environments it persists in association with roaster-derived maghemite (Walker, 2006).

The ESP residue is rich in As_2O_3 (Indian and Northern Affairs Canada, 2007). The next most prevalent As hosts in ESP dust are ROs and Fe arsenates (SRK 2002). Arsenic in ESP dust occurs predominantly as As(III) with some As (V) (Fawcett and Jamieson 2011). ESP dust (not ESP residue as shown in Table 1-1) is the closest proxy available for estimating the composition of actual roaster emissions that effected Giant Mine soils (Wrye, 2008).

Researchers have directly observed As_2O_3 in Giant Mine soils using scanning electron microscopy and micro X-ray diffraction (Wrye 2008; Bromstad 2011). Studies of other As_2O_3-impacted sites have shown in many cases the mineral does not persist for decades as it has at Giant Mine. Yang and Donahoe (2007) examined two industrial sites contaminated with As_2O_3 herbicide in the 1950s and 60s and found that it was no longer present, having dissolved and partially adsorbed onto other species. However, near surface concentrations of total arsenic in outcrop soils at Giant Mine have been observed to range from 156mg/kg to 5760mg/kg with an average of 1546mg/kg, which is higher than the tailings used as backfill in the mine (Bromstad 2011). Most of this arsenic is in the form of arsenic trioxide. It has been postulated that these elevated concentrations are caused by a "wash down effect" where roaster emissions deposited on outcrop surfaces are concentrated in outcrop bowls by rainfall, where they then persist for the long term (Walker 2006).

Giant Mine As_2O_3 is less soluble than similar As_2O_3 deposits found elsewhere. Giant Mine arsenic is likely immobilized for over half the year while the ground is frozen. In addition Sb content (an inherent property of the As_2O_3-rich dust at Giant), greatly influences solubility. Antimony within As_2O_3 can lower As_2O_3 solubility by reducing the thermodynamic activity of As_2O_3 (Riveros *et al.* 2000).

2.1.6 Toxicity

Arsenic is now understood to be a non-essential element with many, but not all compounds being toxic at low concentrations (Rasool *et al.*, 2013). The lethal dose (LD50) for arsenic trioxide is 34.5 mg/kg (in mice) (Bissen & Frimmel, 2003).

Arsenic oxidation state has a significant effect on the mechanism of toxicity. As(V), but not As(III), replaces phosphate in many biochemical reactions because of their electronic structure and properties (Dixon, 1996). Being pentavalent, arsenic is an uncoupler of mitochondrial oxidative phosphorylation. Trivalent arsenicals, including sodium arsenite and arsenic trioxide, inhibit many enzymes by reacting with biological ligands that possess sulfur groups (Hughes, 2002). Mammals are the primary targets of As toxicity mechanistic studies of As toxicity. In mammalian studies As(V), but not As(III), replaces phosphate in many biochemical reactions because of their electronic structure and properties (Dixon, 1996).

Arsenate uncouples in vitro formation ofadenosine-5-triphosphate (ATP) by a mechanism termed arsenolysis. Arsenolysis can occur during glycolysis (the metabolic process to convert glucose to pyrubate). In an intermediate step of the glycolytic pathway, phosphate is linked enzymatically to D-glyceraldehyde-3-phosphate to form 1,3-biphospho-D-glycerate. Arsenate can replace phosphate in this reaction to form the anhydride 1-arsenato-3-phospho-D-glycerate. 1-arsenato-3-phospho-D-glycerate is unstable and quickly hydrolyzes to arsenate and 3-phosphoglycerate, preventing the formation of pyruvate and thus preventing cellular respiration (which requires pyruvate) (Hughes, 2002).

Trivalent arsenicals react with with thiol-containing (R-SH) molecules such as glutathione (GSH) and cysteine (Scott *et al.*, 1993; Hughes, 2002) functional groups. Binding of MMAIII and DMAIII to

these proteins occurs to a greater extent than with the pentavalent organic forms. The binding of trivalent arsenic to critical thiol groups can inhibit important biochemical reactions (Styblo *et al.*, 1997).

Methylation has previously been regarded as a detoxifaction process. Reduction of As(V) to As(III) is now understood to be considered as bioactivation (Cullen *et al.*, 1989). Methylation is a detoxification through accelerated excretion (Gebel, 2002).

2.2 Bioaccesibility Measurements

2.2.1 Diffusive Gradients in Thin Films

The individual chemical species of a single element in a natural solution can include simple hydrated inorganic species, organic complexes, and the element adsorbed to a solid phase. It has been established that the total element concentration is a poor predictor of the impact and behavior that a metal will have on a biological organism (Panther, 2008; Florence *et al.*, 1992). Different chemical species often have varying toxicity, and analysis of a sample for total element concentration is not sufficient to predict toxicity.

Diffusive gradients in thin films (DGTs) are an *in-situ* analytical technique designed to accumulate labile elements in aqueous systems. DGT devices are deployed in an environmental or laboratory setting for a period ranging from hours to weeks. While accumulation of an elemental analyte occurs *in-situ* the concentration is not measured until the DGT is processed in a laboratory setting by an appropriate technique. DGT application has been studied with at least 55 elements (Garmo *et al.*, 2003) with applications found in waters, soils, and sediments.

The DGT technique uses an adsorbent immobilized in a polyacrylamide hydrogel to adsorb analyte species from solution. The binding gel is separated from the solution by a diffusive gel (Panther, 2008).

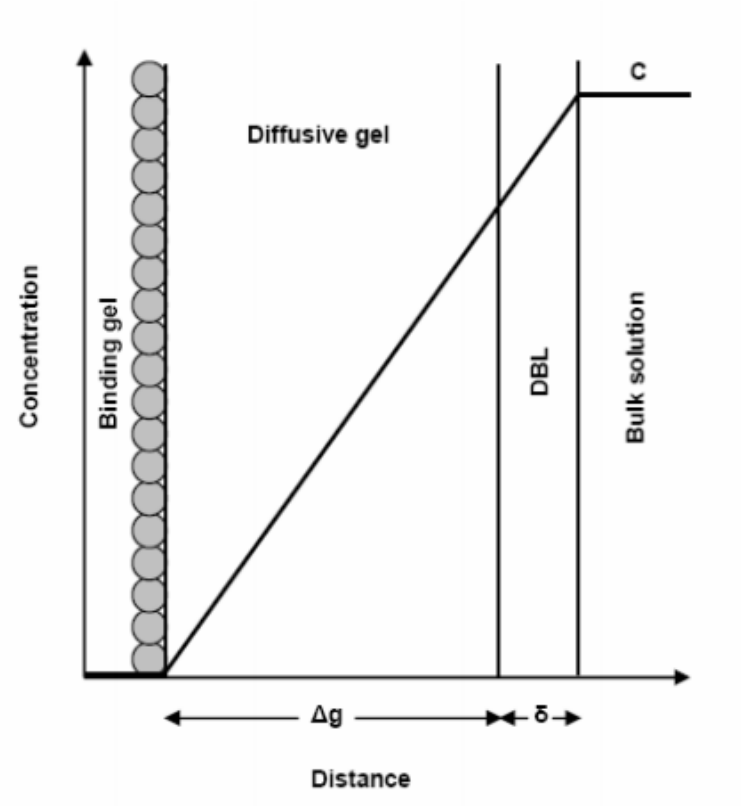


Figure 2-3: Schematic representation of the concentration gradient of a species through a DGT assembly as represented by the bold line where C is the concentration of the measured solution, Δg and δ are the thicknesses of the diffusive gel and the Diffusive Boundary Layer (DBL), respectively). Figure adapted from (Zhang & Davison, 1995)

The DGT technique is based on Fick's first law of diffusion (Zhang & Davison, 1995). The flux, F, of a species to the binding gel is given by the equation below, where D is the element's diffusion coefficient, C is the analyte concentration in the bulk solution, C' is the analyte concentration at the interface between the binding gel and diffusive gel, and Δg and δ are the thicknesses of the diffusive gel and boundary layer.

$$F = \frac{D(C - C')}{\Delta g + \delta}$$

At the completion of a DGT deployment, the binding gel and the diffusive gel are separated and the accumulated analyte is eluted from the binding gel. The concentration, C_e, of analyte in the eluent is then determined by an appropriate analytical technique. The amount of analyte bound to the gel is proportional to the time-average of the labile component of the analyte in solution (Zhang & Davison, 1995).

The diffusive gel controls the overall rate of mass transport to the binding gel. The diffusion coefficient of species within the diffusive gel is usually within 5% of the diffusion coefficient in water (Davlson & Zhang, 1994). Diffusion coefficients are strongly influenced by temperature due to changes in water viscosity. The correction of diffusion coefficient values for temperatures other than 25 °C can be carried out using the equation below where T is temperature (in °C) andD_{25} and D_T are the diffusion coefficients at 25°C and at any given temperature, respectively

$$logD_T = \frac{1.37023(T-25) + 8.36x10^{-4}(T-25)^2}{109+T} + log\frac{D_{25}(273+T)}{298}$$

Correction of diffusion coefficients at different temperature is most important for field applications where temperatures can approach freezing during deployment (Panther, 2008).

Specifically, DGTs measure the free metal ion and metal in labile complexes that can diffuse through the pores of the diffusive gel, and dissociate while travelling through this layer. Metals that do not meet these prerequisites are not measured by the technique because the analyte will not form a stable complex with the adsorbent in the binding layer (Davlson & Zhang, 1994). The final measurement is thus influenced by the adsorbent, the diffusive layer thickness, and the pore size of the gel (Panther, 2008).

For application of DGTs in natural waters the diffusion coefficient of the free metal ion is often used to calculate the DGT concentration (Denney *et al.*, 1999). This is only accurate when complexation of the metal by humic substances is minor. The free ion diffusion coefficient can be significantly higher than the complexed equivalent, which then leads to an underestimation of metal ion concentration. When DGT with an open-pore gel is used to measure metal concentrations in natural water and the contribution of humic substances is unknown, only an "effective" DGT-labile concentration is measured (Panther, 2008).

The influence of unknown humic-influences to DGT measurements can be assessed by using a diffusive gel with a reduced pore size (often referred to as a restricted gel) that significantly decreases the diffusion of humic substances compared to the open-pore gel, but has only a relatively minor effect on the diffusion coefficient of the free metal.

A variety of adsorbents have been used to bind a variety of analytes of interest from solution. Chelex-100 (an iminodiacetate chelating resin) has been used the most extensively to accumulate a variety of metal cations; Ni, Cu, Cd, Zn, Pb, Co, Mn, Ca, Mg, Fe, and Al. Adsorbents have also been mixed together (i.e. Chelex-100 and iron-oxide) to enable the use of a single DGT device to accumulate both anions and cations (Panther, 2008).

When a complex containing the analyte dissociates, the concentration gradient towards the adsorbent ensures that the free metal ion diffuses towards the binding layer and hence diminishes reformation of the complex (Figure 2-3). A proportion of metal from the solid phase will only be available if uptake is rapid compared to diffusional supply. In such a case the depletion of the analytes' concentration in solution in the immediate vicinity of the uptake (ie. roots) causes unsaturation of the analytes' and allows transfer from solid phase to solution. For the component associated with the solid phase to contribute to uptake, it must be capable of rapid transfer to solution (Tusseau-Vuillemin *et al.*, 2004). This solid phase metal is then said to be kinetically labile.

DGTs were used in a bioaccumulation study in *Chrinomus riparius* for Cu, Cd and Pb prediction of metal bioaccumulation in benthic organisms, however in this case total metal concentrations in sediment better predictors of the metal accumulation in the chironomids (Roulier *et al.*, 2008). The relevance of DGTs to estimate the bioavailable fraction of Cu in waters to *Daphnia magna* have been shown to depend on the type of binding organic matter. In laboratory experiments with media spiked with different dissolved organic matter, DGTs are most powerful in estimating the bioavailable fraction of Cu in a humic acid solution (Tusseau-Vuillemin *et al.*, 2004).

2.2.2 Bioavailability

Bioavailability is the fraction of an analyte that is adsorbed by the target receptor. Similarly, but distinctly different, bioaccessibility measures the fraction of an analyte that is available for uptake by a receptor (Doig & Liber, 2000). DGTs measure bioaccessibility. Bioavailability measurements are acquired through *in vivo* experimentation where a receptor is actually exposed to the relevant analyte,

which can be costly and time consuming (Laird *et al.*, 2011). Bioaccessibility measurements do not need to be *in vivo* and are thus preferred when the results can be validated as being relevant to bioavailability measurements

2.2.2.1 Biological Test Methods

Aquatic toxicity tests are used to measure, predict and evaluate effluent of potentially toxic structures. No one test method or organism offers a comprehensive assessment of environmental toxicity of an effluent. Recognizing this, standardization of test protocols based on broadly acceptable toxicity tests measure different toxic end points using organisms representing different trophic levels and taxonomic groups (Environment Canada, 2011). Standardization allows for comparison of dissimilar compounds and results from unaffiliated labs. Testing can be for both lethal and sub-lethal effects.

Most current environmental regulations do not explicitly account for combined effects of chemical mixtures. This is a significant shortcoming in ecological risk assessments. Both lethal and sub-stage tests on standardized test organisms have been used as the basis for generating data for comparing different approaches to predict the toxicity of mixtures of chemicals (Broderius *et al.*, 2005).

The precision of toxicity tests is important for reproducibility. Precision of a seven-day test with fathead minnows was found to have an inter-laboratory coefficient of 31% for survival of larvae and 52% for final weight among 10 U.S. laboratories (Environment Canada, 2011). These tests are precise enough well enough that, in conjunction with careful dosimetry control, complex chemical interactions can be studied. For example, additive toxicity can often be observed in mixtures of chemicals with a common mechanism of action (Broderius *et al.*, 2005).

Chironomus dilutus (formerly known as *Chironomus tentans*) and fathead minnows (*Pimephales promelas*) are two commonly utilized test organisms. Fathead minnows belong to the family Cyprinidae, (carps and minnows) and are native to Canada. A female can produce 1000 to 10000 eggs in a season. Fathead minnows have been used for lifecycle toxicity tests in the U.S. since the 1960s (Mount & Stephan, 1967) and it is now a standard species for acute, sublethal, and chronic effects (USEPA 2002).

Chironomous dilutes has four life stages: egg, larva, pupa and adult. The relevant life stages vary based on the type of test being performed, and can vary from just one to all four. A single female can lay an egg mass containing an average of 2300 eggs at optimal conditions. *Chironomous dilutes* larvae live in the top few centimeters of sediment and occasionally up to 40cm depth.

2.2.2.2 DGTs and Toxicity Tests

DGTs have been used in conjunction with toxicity tests to assess toxicity (measured as EC50 or other endpoints) and uptake in exposed organisms through analysis of contaminant labile fractions. In an experiment with wastewater effluent containing an atypical distribution of dissolved organic material (DOM) was found to have a protective effect that was reflected by DGT measurements. DGTs were shown to approximate copper toxicity in an unnatural system with high DOM, though the statistical relevance was not reported (Pernet-coudrier *et al.*, 2008).

Other studies have also shown that, depending on the nature of DOM, and the species of interest DGT measurements can overestimate toxicity. In a study of copper binding to fish gills DGT measurements of labile Cu concentration was twice the labile Cu concentration as measured by ISE (Ion Selective Electrode). Correlation of DGT-labile Cu with gill Cu was still statistically relevant ($P < 0.0001$) and thus useful as an empirical predictor of Cu bound to fish gills (Luider et al., 2004).

In a study where toxic effects were absent in low concentration water samples DGTs were uniquely employed to pre-concentrate labile contaminant fractions and re-conduct the tests on the resulting extract. Roig et al. (2011) eluted DGT binding gels to concentrate their analytes, then neutralized the acidic eluent with NaOH to a new solution of toxicity testing. Toxicity testing was conducted on *Pseudokirschneriella subcapitata* and a statistical correlation was found between the DGT extracts' toxicity and the DGT concentrations ($p < 0.01$; $r > 0.5$) (Roig *et al.*, 2011).

2.3 Summary

Arsenic is a highly toxic metalloid with a variety of factors contributing to the overall As risk and toxicity posed to exposed environments and organisms. Arsenic at Giant Mine exists in a variety of

phases and tailings streams contained both low (arsenopyrite) and high (As_2O_3) As loadings. Proper characterization of As sediments must address the variety of factors that affect overall bioavailability and identify influences that may change conditions such as mineral phase sequestrations over time.

Biological exposure test methods are useful for quantifying the effect of specific As-rich sediments on specific organisms. DGTs are a method of measuring labile metal/metalloid concentrations that accounts for the presence of humic acids. DGT measured-As concentration and other methods of measurement such as mini-peepers have been correlated to uptake in toxicity tests in previous research.

Chapter 3

Characterization of arsenic in contaminated sediments and waters at Giant Mine, Yellowknife, NWT with comparison to bioaccumulation in *Chironomus dilutes* and *Pimephales promelas*

3.1 Introduction

The legacy of Giant Mine is an example of the complex mobilization of natural, bedrock hosted, arsenic (As) into more available and environmentally sensitive hosts such as water, soil, sediment and tailings. This mobilization occurred during the mining and processing, including roasting, that was required for processing the arsenopyrite-bearing refractory gold-ore.

Mine production began in 1948 when ore was processed by crushing, grinding, froth floatation and mercury amalgamation. This process only extracted the limited free gold found in the ore and missed the refractory gold which made up the majority. From 1949 to 1999 ore was processed by roasting an arsenopyrite concentrate produced by flotation and then leaching the resultant calcine with cyanide. Roasting was required to make the sulfide concentrate amenable to cyanidization.

In addition to As, several metal/metalloids were mobilized during mining. Figure 3-1 illustrates the enrichment in As, Pb, Sb, Zn, and Cu sediment concentrations in Yellowknife Bay due to contamination from mine waste inputs.

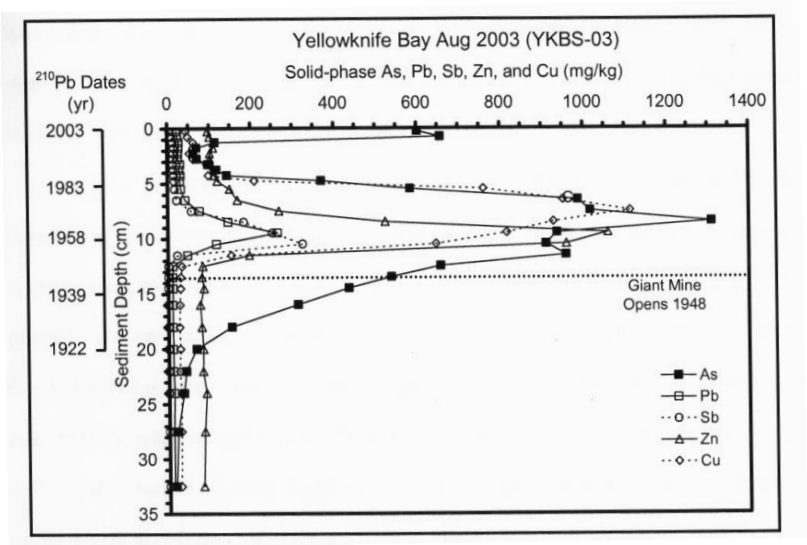


Figure 3-1: Vertical metal/metalloid concentrations in Yellowknife Bay and the 210Pb timeline illustrating the release due to the start of mining (Andrade, 2006).

Three waste streams with distinct chemical and physical properties compose the bulk of the tailings. These include flotation tailings, cyanided calcine residue and roaster dust/precipitate. Flotation tailings are high tonnage and low As, which is primarily present as arsenopyrite. Calcine (roaster waste that includes As hosted in iron-oxides) and roaster dust (As hosted in As_2O_3) are lower tonnage but have higher As concentrations as roasted products of the sulfide concentrate. Roaster dust was deposited aerially in the surrounding environment and captured by baghouse and precipitator technology. Changes within these streams occurred over time as milling, processing, and precipitator technology and practices advanced.

The complicated solid-phase mineralogy of the waste streams affects the mobility and resulting toxicity of the As within. Mineral form, oxidation state, particle size, encapsulation in other minerals and solution Eh and pH all affect the release of As in aqueous systems. Furthermore, aqueous speciation and other solutes, such as organic ligands, affect As uptake and toxicity. Total As concentrations in soil and sediments are not necessarily indicative of As bioaccessibility or As toxicity.

The fraction of total As or other contaminant that is available for absorption into an exposed organism is termed the *bioaccessible* fraction. Bioaccessibility is an operationally defined measurement, meaning that it can be measured by different methods, which may result in different values that may not

be comparable (Fendorf *et al.*, 2004). Total dissolved metals in pore-water have been correlated to toxicity and uptake in benthic organisms and can be considered measure of bioaccesibility. Bioavailability is the fraction of As or other contaminant that is actually absorbed by an exposed organism (Ruby *et al.* 1999).

Labile metal/metalloid concentration, which is generally less than total concentration, can be considered the bioaccessible fraction in contaminated systems. Labile metals/metalloids do not include dissolved elements that are strongly bound by strong ligands which inhibit uptake in fish and DGTs diffusive gradients in thin films (DGTs).

While humic and fulvic acids are best known for binding dissolved cationic metals they also complex with As which exists as an anion. Arsenic interaction with humic acid is strongly pH dependent due to speciation effect of pH on the polyprotic As anion. At neutral pHs As(III) exists as the neutral $As(OH)_3$ and As (V) exists as the charged anions $HAsO_4^{2-}$ and $H_2AsO_4^{2-}$. At this pH humic acid binds binda 6-10 times more As(V) than As(III) (Buschmann *et al.*, 2006).

Arsenic complexes of hard inorganic ligands such as chloride or carbonate are weaker in comparison to soft ligands such as sulfide. Humic acids are complex mixtures and the mechanism that binds As is believed to be a variable combination of carboxylic, phenolic, and sulfhydryl bonds which are known to interact with As. These are believed to be ligands which most strongly bind As and prevent measurement by DGTs and uptake by exposed organisms. Humic acid is believed to also bond to As via ternary complexation mechanisms (ie. humic acid−cation−As) though these mechanisms have been less thoroughly studied.

The portion of total As that is actually be absorbed by an exposed organism is the *bioavailable* fraction (Ruby *et al.* 1999). Bioavailability is measured during *in vivo* animal dosing studies (Plumlee and Ziegler 2007). Total concentration of an element is usually greater than the bioaccessible and bioavailable fractions. Thus, total concentration of As in sediments at Giant Mine does not give enough information to understand the relative risk to exposed organisms.

The primary research objectives of this are is to investigate solid phase As hosts in impacted sediments of Giant Mine and to measure bioavailable As (DGTs, mini-peepers, surface water) and determining which methods best correlate and predict element uptake. Specifically, this research will:

- Conduct detailed sampling and characterization of the co-existing sediment, pore-water and surface water, including aqueous and solid phase As speciation, at three selected sites.
- Examine the relationship, if any, between sequential extractions and pore-water concentrations.
- Measure sediment toxicity using *Chironomus dilutes* and *Pimephales promelas* model organisms.
- Measure sediment labile and bioaccessible metal/metalloid concentrations using thin films (DGTs), mini-peepers (dialysis cells) and surface water concentrations.
- Use statistical analysis to rank DGTs, mini-peeper, and surface water concentrations on their capacity to predict toxicity and uptake in the model organisms.

3.1.1 Arsenic Toxicity

Arsenic is now understood to be a non-essential element with many, but not all, As compounds toxic to humans at low concentrations. The lethal dose (LD_{50}) for As_2O_3 is 34.5 mg/kg in mice (Broderius *et al.*, 2005).

In solution, the oxidation state of As has a significant effect on the mechanism of toxicity. Mammals are the primary targets of As toxicity mechanism studies. In mammalian studies As(V), but not As(III), replaces phosphate in many biochemical reactions because of their electronic structure and properties . As(V) uncouples mitochondrial oxidative phosphorylation through one of its most well-known mechanisms of toxicity. As(III) compounds, including As_2O_3, inhibit many enzymes by reacting with biological ligands that possess sulfur groups . These unspecific mechanisms of toxicity are believed to occur in aquatic animals in addition to other forms of toxicity. For example, including oxidative stress in gills. Most As(III) compounds, with the exception of some organic species, are more toxic than As(V)

.

3.1.1.1 Biological Test Methods

Toxicity tests are used to measure, predict and evaluate potentially toxic sediments, effluent and other wastes. A wide variety of organisms are used in these tests as no one test method or organism offers a comprehensive assessment of environmental toxicity. Standardization of test protocols based on broadly acceptable toxicity tests measure different toxic end points using organisms representing different trophic levels and taxonomic groups (Environment Canada, 2011). Standardization allows for comparison of dissimilar compounds and results from unaffiliated labs. Testing can be for both lethal and sub-lethal effects.

Both lethal and sub-lethal tests on standardized test organisms have been used as the basis for comparing different approaches to predict the toxicity of chemicals (Broderius *et al.*, 2005). The precision of toxicity tests is important for inter-laboratory reproducibility, precision of a seven-day test with fathead minnows was found to have an inter-laboratory coefficient of 31% for survival of larvae and 52% for final weight among 10 U.S. laboratories (Environment Canada, 2011). These tests are precise enough that complex chemical interactions can be studied. For example, additive toxicity can often be observed in mixtures of chemicals with a common mechanism of action (Broderius *et al.*, 2005).

Chironomus dilutus (a common midge) and fathead minnows (*Pimephales promelas*) are two commonly utilised test organisms. Fathead minnows belong to the family Cyprinidae, (carps and minnows) and are native to Canada. Fathead minnows have been used for lifecycle toxicity tests in the U.S. since the 1960s (Mount & Stephan, 1967) and it is now a standard species for acute, sublethal, and chronic effects (USEPA 2002).

Chironomous dilutes has four life stages: egg, larva, pupa and adult. The relevant life stages vary based on the type of test being performed, and can vary from just one to all four. A single female can lay an egg mass containing an average of 2300 eggs at optimal conditions. *Chironomous dilutes* larvae live in the top few centimeters of sediment and occasionally up to 40cm depth (Environment Canada, 2011).

3.1.1.2 Bioavailability measurements - DGTs

Diffusive Gradients in Thin films (DGTs) are designed to accumulate labile species in both environmental and laboratory systems. DGTs can be deployed in surface waters and saturated sediments. The DGT technique uses an adsorbent immobilized in a polyacrylamide hydrogel to adsorb analyte species from solution. The binding gel is separated from the bulk solution by a permeable and diffusive gel.

DGTs deployed in in soils and sediments account for the ability of solid phase to sustain the pore solution concentration following depletion by uptake. A proportion of metal in sediment systems will only be available from the solid phase if biota uptake is fairly rapid compared to diffusional supply, if biota presence and activity depletes metal concentration faster than osmosis and diffusion resupplies it. Depletion of its concentration in solution in the immediate vicinity of the biota allows transfer from solid phase to solution. For the component associated with the solid phase to contribute to uptake, it must be capable of rapid transfer to solution, a property not assessed by bulk chemistry data.

When deployed in surface water, DGTs are useful for accounting for the formation of organic-metal complexes that are not readily transported across cell membranes and are thus less available to organisms. Fulvic and humic acids form complexes that are strong for some metals and fairly weak for others, but because they are often abundant, their presence results in the dominance of organic complexes in many natural waters (Zhang & Davison, 1995,Warwick *et al.*, 2005).

Despite the known impact of humic acid on As speciation and mobility, data on the binding behavior of As(III) and As(V) with humic acids is less available compared to other elements (Buschmann et al. 2006). DGTs can measure labile As concentration as well as cationic metals, though a separate binding gel is required. Cationic metals are bound by a Chelex© gel, while both As(III) and As(V) species are bound with an Fe-oxide gel (Österlund *et al.*, 2010) .

3.2 Site Locations

The three sites sampled for this study, Baker Pond, Yellowknife Bay Beach and Baker Creek Outlet, are shown on the map below.

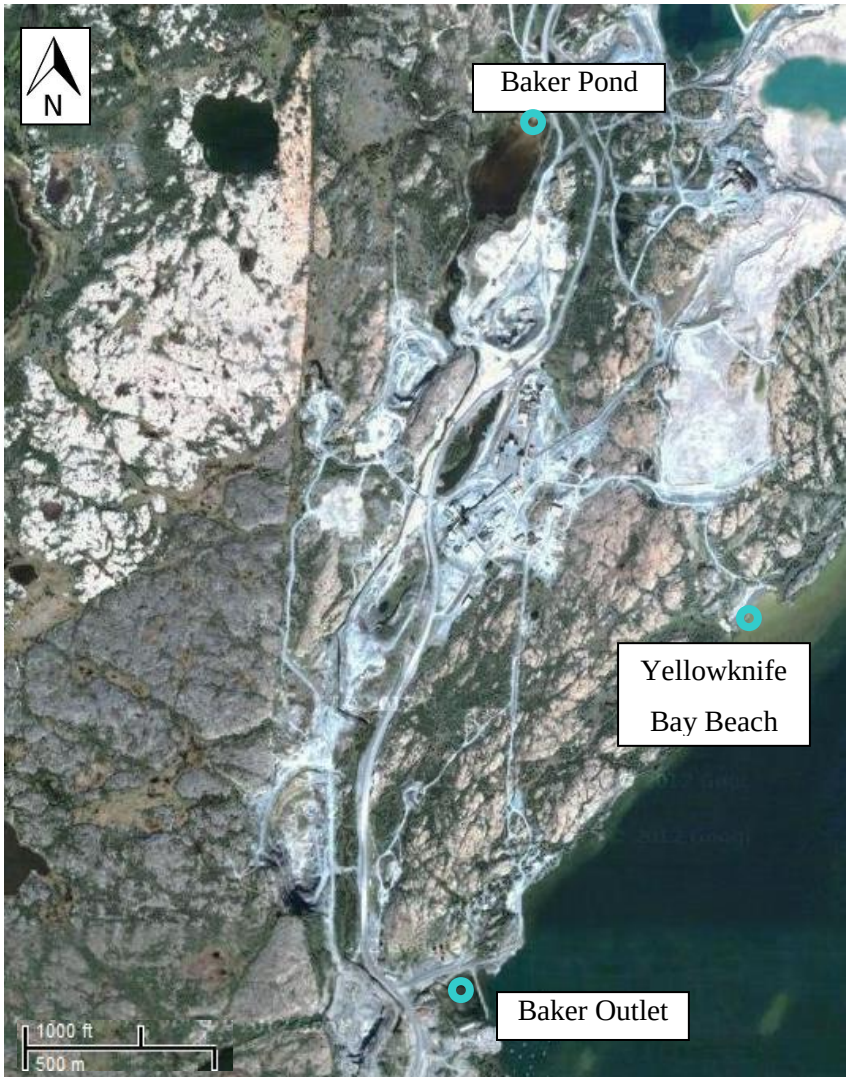


Figure 3-2: A map of Giant Mine illustrating the locations of the three sites.

3.2.1 Baker Pond (N 62°30.556' W 114°21.460')

Baker Pond is a natural body of water that lies downstream of the settling and polishing ponds used for the water treatment plant which processes mine-water infiltration. Starting in 1951, a mixture of calcine and fine-grain tailings was deposited onto the northernmost portion of Baker Pond known as Jo-Jo Lake (SRK Consulting, 2005). Recent work has established that the As bearing sediment at this site is primarily calcine (Fawcett, 2009). Prior to the opening of the water treatment plant in 1981 and the

implementation of better sedimentation controls, significant amounts of sediments also flowed over ice-covered dams in the spring and were deposited in the northern section of Baker Pond (Fawcett, 2009).

Much of the nearby tailings have recently been covered by a cap to limit surface exposure as part of an initiative to install "mitigative measures to permanently remove the potential of these tailings from coming into contact with the water" of Baker Pond (Golder Associates, 2011). The installation of this covering was mostly completed by December 2011 (Aboriginal Affairs and Northern Development Canada, 2012b), however efforts to vegetate some of the covering have been unsuccessful and ongoing since as late as April, 2012 (Aboriginal Affairs and Northern Development Canada, 2012a). The capping process included a silt curtain around a portion of the perimeter of Baker Pond (Golder Associates, 2011), but it did not extend to the site.

Sampling of nearby Baker Pond sediments by previous researchers measured As concentrations ranging from 800 mg/kg to 2000 mg/kg in sediment and pore-water concentrations ranging from 2 ppm to 60 ppm (Fawcett, 2009). This sampling site was specifically chosen to be near that of Fawcett (2009) in order to further examine some of the most As rich sediments observed at Giant Mine. A separate assessment of Baker Creek included sampling and toxicity testing of sediments acquired somewhere in the vicinity of this sampling site (exact coordinates not supplied recorded, but within Baker Pond) measured surface sediments to have 1870 mg/kg As (Golder Associates 2011b).

Figure 3-3: The Baker Pond sampling site, which is marked by the white arrow. The rubble covers the curtain, which does not continue past the beginning of the vegetation.

3.2.2 Yellowknife Bay Beach (N 62°29.819' W 114°20.734')

The shore of Yellowknife Bay of Great Slave Lake was used as a tailings disposal site for the mine during its first years of operation from 1949 to 1951 (Bromstad & Jamieson, 2012). These historic tailings have experienced strong erosional forces, spreading out to an area over twice their original size (SRK Consulting, 2004). Recent study of the area was conducted in deeper sediments of Yellowknife Bay (Andrade et al., 2010). I sampled close to shore in order to maintain consistency in the depth of the sediments across all sites.

Figure 3-4: The Yellowknife Bay Beach sampling site, marked by the white arrow, just outside of the sparsely vegetated area along the beach.

3.2.3 Baker Creek Outlet (N 62°29.248' W 114°21.707)

A breakwater built in 1964 causes deposition of fine river sediment in Baker Creek before it flows out into Yellowknife Bay. My site is located within the vegetated area of the outlet, where sediment has been preferentially deposited and there is little surface water flow.

Historic spills, notably decanting of tailings ponds in the spring, have released contaminants to Baker Creek that were then carried downstream to my sample site. Such spills were often poorly recorded. More recent events have been recorded and carefully investigated. For example, on May 14th 2011 an ice dam formed in Baker Creek that caused flooding into the tailings before flooding back out. In response a monitoring plan was set up which determined that contaminant and metal levels in Baker Pond had returned to previous levels within two weeks and within one week at Baker Creek outlet (Mackenzie Valley Land and Water Board, 2011).

In 2002 it was calculated that 1096kg of dissolved As was flowing through the mouth of Baker Creek Outlet over a period of one year (SRK Consulting, 2002). Previous measurements of the sediment at Baker Creek Outlet have revealed highly concentrated As concentrations ranging from 278mg/kg to 2661mg/kg throughout the outlet (Mace, 1998; Fawcett, 2009; Stephen, 2011).

Figure 3-5: The Baker Creek Outlet sampling site, as marked by the white arrow.

3.3 Sampling Methods

3.3.1 Waters

Surface water was collected from each site. Surface water at each site was approximately 30cm deep. A 2L High Density Polyethylene (HDPE) bottle was triple rinsed with the surface water and a grab sample was taken. Care was taken to avoid suspended debris.

Yellowknife Bay (south of the Yellowknife Bay Beach samplings site) was selected for use as reference water because it was geographically near the sample sites and considered to be representative of Great Slave Lake. Forty liters of reference water was collected in two triple-rinsed 20L Low Density Polyethylene (LDPE) cube containers while taking care to avoid suspended debris.

At each sampling site pore-water was collected by installing suction lysimeters to a depth of 10cm. Suction lysimeters were then left for 24 hours to allow disturbed pore water to equilibrate with the solid phase. A partial vacuum (10 centibar) was then manually pumped and, after an additional 24 hour period, the lystimeter was sampled.

The surface and pore water from each site were analyzed for their trace metal, cation, anion, and arsenic speciation concentration. Water used for trace metal and cation analysis were filtered using 0.2µm Acrodisc® syringe filters and acidified with HNO_3 to pH 2. Water for anion analysis was also filtered but left unacidified. Preservation of arsenic As(III)/As(V) can be complicated as various methods are superior depending on the type and concentration of the other solutes (McClesky et al, 2004). Water for As measurement was conducted in triplicate. Filtration followed by acidification with HCl, freezing, or no preservation was done.

3.3.2 Solids

Sediments were collected as bulk grab samples and vertical cores. At each site the core samples were taken before the bulk sample to prevent the disturbed bulk sediment from contaminating the top of the cores. Grid-based sampling was not used at any site. Several kilograms of sediment were required from each site and grid-based sampling methods were inappropriate for high volume sampling

Sediment cores were taken by manually driving 7.6cm wide and 60cm long Lexan® polycarbonate cores into the sediment and digging out the sediment around them for retrieval. Sediments were too fine grained too simply cap the cores and pull from above. If a rock or other obstruction was hit during the insertion of the core, the tube was retrieved, washed, and reinserted approximately adjacent to the first attempted site.

Bulk sediment was collected using a trowel and placing the sediment into plastic bags. Sediments were taken from no deeper than 15cm, the goal being to take sediments representative of the depths that benthic invertebrates inhabit and the lysimeters sampled.

3.4 Analytical Methods

3.4.1 Waters

3.4.1.1 Field Parameters

A YSI multi-meter (version 556 MPA) was used to measure field parameters of temperature, pH, eH, DO and specific conductance of the water samples *in situ*. The probe was calibrated each day with pH 4, 7, and 10, Zobell's solution, distilled water, and KCl solution standards for pH, pE, $O_{2(aq)}$ and specific conductance measurements, respectively. Measurements were recorded instantly for surface water measurements and within minutes of collection for pore water. Alkalinity was measured in the field using the bromcresol green-methyl red indicator with a HACH digital titrator (Model 16900).

3.4.1.2 Anions and Cations in Water Samples

All water chemical analysis were completed by the Analytical Services Group at CanmetMINING. Anion were separated by high pressure liquid chromatography (HPLC). The separator column used a packed methacrylate based anion-exchange resin (IonPac Analytical Column AS14). Following separation Cl^-, NO_3^-, PO_4^{-3} and SO_4^{-2} were measured using conductivity and UV sensors.

Ca, Fe, K, Mg, Mn, Na (and high As concentrations) concentrations in surface and pore-water were by measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS. As, Co, Cr, Cu, Mn, Ni, Pb, Sb and Zn trace metals were analyzed using the ASG's internal test method 3VIXXX1 on a Varian Viasta ICP-AES.

3.4.1.3 Arsenic Speciation in Water

As(III)/As(V) speciation was measured using an HPLC-ICP-MS system. Solutions for As(III)/As(V) analysis were diluted with 2 mM Na_2EDTA (disodium ethylenediamine tetraacetate) solution in order to transform As(III) to anion $As(EDTA)^-$ in solution. Then, the diluted solutions were injected onto an anion-exchange column. After separation by HPLC (ICS-3000 Dionex) on a packed

methacrylate based anion-exchange resin the As anions were quantified by ICP-MS (Perkin Elmer Elan 6100 DRC).

Three forms of preservation of As species were used because of the uncertainties associated with individual preservation methods. Conventional acid preservation, freezing, and refrigeration were tested.

Conventional acid preservation with HCl to pH 2 is most commonly used. In acidic conditions oxidation-reduction reactions of As are often slowest and iron oxide precipitation reactions are limited, thus preventing precipitation of As and changes in pH (Samanta & Clifford, 2006). However, acidification can cause As-sulphur phases to precipitate and has been observed at 1290mg/L sulfate and 1.8mg/L As . Because of this, freezing to -4°C was used as another method of preservation. Freezing is expected to slow reaction rates, limit oxygen diffusion and prevent altered adsorption behavior from pH changes (Planer-Friedrich *et al.*, 2007). Freezing is an inappropriate preservation method when samples contain high Fe as Fe phases can precipitate, even in the frozen form (DeSisto, 2008).

3.4.2 Solids

3.4.2.1 Bulk Sediment Chemistry

Sediments were dried under a nitrogen atmosphere to prevent oxidation and homogenized by manual mixing. Four gram sub-samples of bulk sediment were sent to ACME Analytical Laboratories, Vancouver, BC for determination of bulk chemistry. Three subsamples were taken from each sample to test for homogeneity. All samples underwent ultratrace *aqua regia* digestion (package 1F-MS, ACME Catalogue 2007) in a solution followed with analysis by ICP-MS (Perkin Elmer 6000 or 9000) for a basic 37-element suite (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Te, Th, Ti, Tl, U, V, W, Zn). These results contained three subsamples which had As concentrations above the limit of quantitation (10,000 ppm). These samples were then re-analyzed by ICP-AES by Queen's University Analytical Services Unit.

3.4.2.2 Sequential Extractions

Sequential extractions were conducted according to the BCR (Community Bureau of Reference) three-stage extraction procedure(Quevauviller *et al.*, 1994). The four following stock solutions were prepared for the extraction:

- Solution 1 (acetic acid, 0.11 mol/L): diluted from glacial acetic acid.
- Solution 2 (hydroxylamine hydrochloride, 0.1 mol/L): hydroxylamine hydrochloride dissolved in water and acidified with concentrated HCl acid to pH 2.0.
- Solution 3 (hydrogen peroxide, 30%): hydrogen peroxide was used as supplied by the manufacturer i.e. acid-stabilised to pH 2.0±3.0.
- Solution 4 (ammonium acetate 1.0 mol /L): ammonium acetate dissolved in water and acidified with nitric acid to pH 2.

The extraction was performed in 100ml centrifuge tubes using a mechanical shaker in a room at roughly 25°C. Three extractions were performed using the four solutions.

Step 1: 20 ml of solution 1 was added to 250 mg of sediment in a centrifuge tube and shaken for 16 h at room temperature. The extractant was separated from the solid residue by centrifugation at 1500 g and decanted decantation of the supernatant liquid into a high density, polyethylene container.

Step 2: 20 ml of solution 2 was added to the remaining sediment from Step 1 in the centrifuge tube, and the extraction was performed as described above.

Step 3: 10 ml of solution 3 was added carefully, in small aliquots to avoid losses due to violent reaction, to the residue from Step 2 in the centrifuge tube. The centrifuge tube was then shaken for 16 h at room temperature. The digestion was continued by heating the covered tube for 1 h at 85 °C and the volume reduced to a roughly 4 ml. A further aliquot of 20 ml of solution 4 was added to the residue, which was then shaken for 16 h and separated from the sediment by centrifugation.

3.4.2.3 Environmental Scanning Electron Microscope (ESEM)

Thin sections were examined under low vacuum with an environmental scanning electron microscope (ESEM) using the back-scatter electron (BSE) detector on the MLA 650 FEG ESEM at Queen's University. Thin sections were not carbon-coated in order to allow for further analysis using synchrotron techniques. ESEM analysis is useful for finding As hosts in Giant Mine sediment samples

because the BSE detector the BSE detector returns As-bearing grains in high contrast to most other minerals. Arsenic often has the highest atomic number present, thus appearing much brighter than non-As bearing minerals. As_2O_3, shown below, strongly stands out against the background. Arsenic trioxide was the only mineral observed to suffer beam damage during analysis.

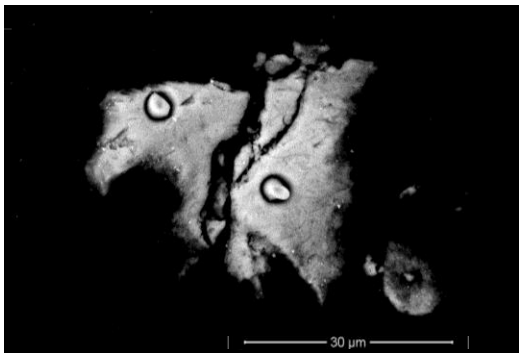


Figure 3-6: An As_2O_3 grain viewed on the MLA 650 FEG ESEM under low vacuum. Note the two ablation circles caused by the beam.

3.4.3 Synchrotron Techniques

All synchrotron analyses were performed at Brookhaven National Lab, National Synchrotron Light Source on beam lines X26a and X11.

3.4.3.1 Micro-X-Ray Fluorescence (µXRF) Mapping

Targets selected by the ESEM were mapped for element concentrations prior to µXRD and µXANES analyses. Due to the uncertainty involved in finding targets using the optics at the synchrotron, µXRF was used to find and confirm the choice of ESEM targets. µXRF mapping can be used in "fly-scan" mode that records a XRF spectrum at each point in a map, using an automated stage to allow for fast acquisition. µXRF mapping allows relative element concentrations across an area of interest to be visualized and has extremely high sensitivity.

3.4.3.2 Micro X-Ray Diffraction (µXRD)

Arsenic host mineralogy was determined using 2-dimensional (2-D) µXRD images from a Bruker SMART 1500 CCD area detector. Data was collected for 60s at 17479 eV and wavelength 0.7039 Å. 2-D images were analyzed and integrated in the computer program Fit2D (Hammersley *et al.*, 1996), which was calibrated using a mixture of two standard reference materials, α-Al_2O_3 and silver behenate

($AgC_{22}H_{43}O_2$). Care was taken to distinguish between smooth and spotty Debye-Scherrer rings. Smooth rings correspond to nanometer sized particles with random orientation, and bright, spotty rings are indicative of submicron particles with reduced random orientation (Walker *et al.*, 2005). Once 2-D images were integrated into 1-D diffraction pattern images in Fit2D. 1-D patterns were analyzed in the peak matching software XPert High Score Plus against its reference pattern database.

3.4.3.3 Micro-X-Ray Absorption Near Edge Structure (μ*XANES*) and bulk XANES

Micro-XANES analyses were performed by scanning across the As Kα absorption edge range (11800 eV to 12000 eV). The range was divided into three sections with different step sizes (eV) and dwell times (1s to 4s) to optimize data quality and collection time. Step sizes were 5 eV in the pre-edge range, 0.4 eV over the edge, and 2 eV in the post-edge range. Three standards were chosen to cover As oxidation states from As(-I) to As(V): arsenopyrite (-I), As2O3 (III), and scorodite (V). Standards were made by grinding standard material to a powder, suspending it in ethanol, and mixing the suspended fraction with boron nitride (2% As w/w) in order to create a homogenous diluted film of consistent concentration that would not saturate the detectors. This was then spread thinly on a piece of Kapton® tape for analysis at the synchrotron beamline. The scorodite standard was run periodically with μXANES to monitor energy shifts (usually > 0.5 eV) over time. XANES spectra were analyzed in the program SIXPACK. Standard and unknown spectra were normalized and pre-edge and post-edge corrected to remove background. After this, unknown absorption edges were determined and any calibrations necessitated by changing scorodite drift standards were performed. SIXPACK was then used for linear combination fitting to fit unknown spectra to the three standards used and to assign a percentage value to each As oxidation state present.

3.4.4 Toxicity Tests

3.4.4.1 *Chironomus dilutus* 10 day toxicity test

Chironomus dilutus (a non-biting midge), formerly known as *Chironomus tentans*, were raised from eggs on the bulk sediment collected from each site according to the procedures given by

Environment Canada (Environment Canada, 2011). Juvenile *C. dilutus* were obtained by collecting eggs from a culture of mature adults maintained at CanmetMINING. The eggs were kept in dechlorinated and filtered tap-water until they hatched, at which point they were transferred into a sand tank and fed ground TetraMin® slurry (commercially available fish food) until they reached ten days of age. Ten day-old chironomids were then and were placed in beakers containing 150ml of bulk sediment and 300ml of water with each treatment receiving then individuals. After 10 days of exposure to the sediments the *C. dilutes* were manually retrieved from the beakers. Sieves were used to ensure that no organisms were missed. They were held for 24hrs in clean dechlorinated water to ensure gut clearance of ingested sediment. They were anesthetised with clove oil prior to being dried then weighed. The endpoints used for measuring toxicity were survival rate, tissue mass, and tissue metal concentration. Tissue concentrations were determined by dissolving the dried tissues in 70% nitric acid at 60°C, adding hydrogen peroxide after digestion and submitting the dissolved *C. dilutes* to ASG at CanmetMINING for analysis.

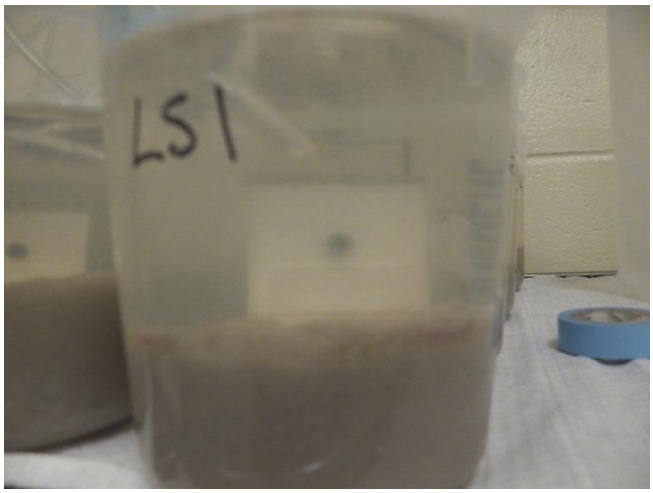


Figure 3-7: A beaker containing a peeper, control sediment, and *chironomids*. The *chironomids* can be seen as the thin red lines at the SWI. Only one of the two peeper chambers can be seen.

3.4.4.2 *Pimephales promelas* 21 day toxicity test

Pimephales promelas (fathead minnows) eggs for the toxicity tests were obtained from a culture maintained at CanmetMINING. Adult fish were placed in tanks with a ratio of 2:4 male:female fish and exposed to temperature ($25^{o}C$ +/- $1^{o}C$) and food (blood worms/brine shrimp) conditions that would

induce them to breed. The tanks were checked daily for eggs and any new eggs were removed and placed in a hatching tank for 24hrs to allow them to water harden at which point the eggs were removed gently from the tile and used for testing.

Testing involved exposing fathead minnow eggs and larvae over a period of 21 days in a method adapted from (Colavecchia *et al.*, 2004). Each cone test chamber (seen below) contained 150ml of sediment and 850ml of reference water. Twenty eggs (~24h-old) were suspended in the overlying water in a screened dish and observed daily for mortality. After hatching (~3-4 days) larvae were fed live juvenile brine shrimp twice daily for a total exposure period of 21 days. Air bubblers were placed inside the cones to oxygenate the water. The bubblers were maintained throughout the test to prevent toxic levels of ammonia from accumulating. Each sediment exposure was conducted in triplicate. The exposure test assessed the development of the fathead minnows to contamination of water above the sediment.

The test is designed to mimic environmental conditions by allowing the bulk sediment from each cone to equilibrate with the water column for 10 days prior to adding organisms. This is done to allow time for the prevailing redox conditions to re-establish in the lab.

At the end of the test fish were anesthetised, dried and measured for metal content using the same procedure as the *Chironomus dilutus* test procedure. The endpoints used for measuring toxicity was mortality, dry tissue mass, and tissue metal concentration.

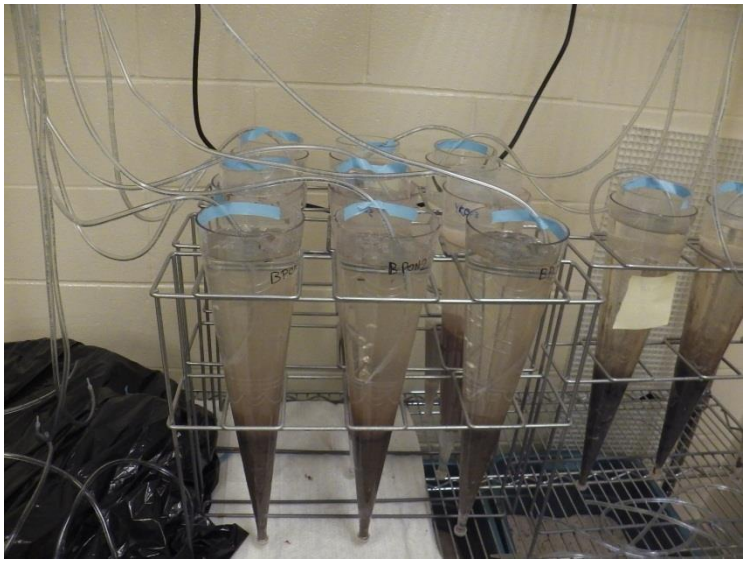


Figure 3-8: The fathead minnow tests being conducted. Each row of cones holds the replicate sediments from a sample site.

3.4.4.3 Dialysis Cell (Mini-Peepers)

Shown below, mini-peepers were placed in the *chironomid* test beakers during testing to capture representative pore water and surface water samples. "Mini-peepers" are dialysis cells containing Milli-Q© purified water stored behind a diffusive membrane that allows for exchange of the laboratory water with the desired solution.

Filter paper (0.2µm) was cut to size and unassembled mini-peepers were cleaned in 15% nitric acid and triple rinsed with Milli-Q© purified water prior to assembly. The mini-peepers were then filled with Milli-Q© water and the filter paper gently placed on top. The filter was fixed in place by screwing the front plate of the mini-peeper into place. The assembled DGTs were then stored in Milli-Q© water under nitrogen bubbling to deoxygenate for the 24 hours prior to deployment in *Chironomus dilutus* beakers for 10 days.

Peepers were extracted at the end of the *Chironomus dilutus* toxicity tests to prevent disturbing the beakers during the tests. Two milliliters of water was extracted from each peeper chamber by creating a hole in the membrane with a micropipette. Chemical analysis of the waters was done by the ASG at CanmetMINING.

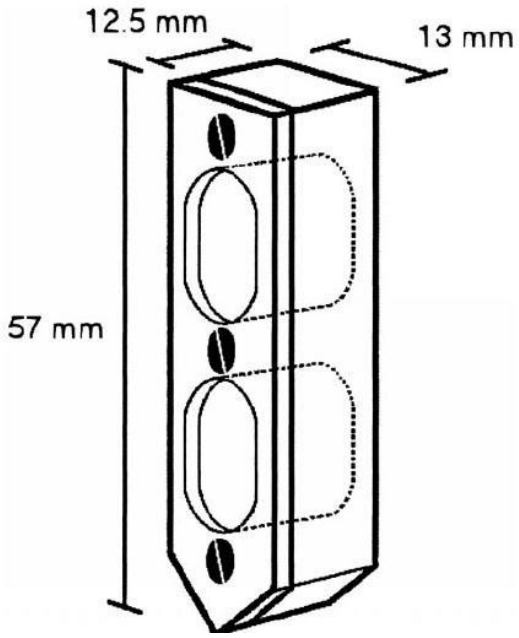


Figure 3-9: A diagram of the minipeeper as seen in Figure 9. The minipeeper is installed so that the SWI is between the top and bottom chamber, thus allowing for measurement of surface and pore water.

3.4.4.4 Diffusive Gradients in Thin Films (DGTs)

Two binding gels in DGTs were utilized for analysis of labile metals and As in the *Pimephales promelas* 21 day toxicity test. A Chelex© resin gel was used for binding of cationic metals and an iron oxide impregnated gel was for As analysis. The iron-oxide binding gel adsorbs As(III) and As(V) through inner-sphere complexation reactions with replacement of hydroxyl groups on the surface of the iron-oxide. Below the saturation limit of the Fe-oxide for As (0.1mg) there is no competition between As(III) and As(V) for sites (Panther, 2008). All DGT measurements were below this threshold though Baker Pond values did approach it (0.087mg).

Unassembled DGTs were cleaned with 15% nitric acid and triple rinsed with Milli-Q© purified water prior to assembly. Assembly was completed by hand using similarly cleaned plastic spatulas and tweezers. DGT pistons were left facing up in and the binding gel manipulated to lie flat on top. The diffusive gel was then placed on top of the binding gel and capped with a filter (0.2µm). The DGT cap

was then placed on top and sealed with pressure. Assembly was conducted in a ventilated fume hood to prevent contamination with dust.

The assembled DGTs were deoxygenated in a 0.01 M NaCl solution bubbled with nitrogen for 24 hours before deployment. One of each DGT was placed in *Pimephales promelas* 21 day toxicity test 10 days. The DGTs were held in place by zip ties.

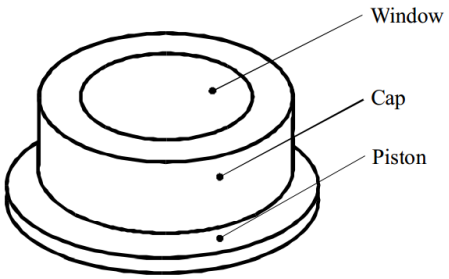


Figure 3-10: A diagram of a water DGT. This form of DGT utilises the same layering of a membrane, diffusive gel, and resin gel, as the sediment DGT.

DGTs were retrieved at the completion of the toxicity tests. The piston and cap were separated manually, taking care not to damage the binding gel. The binding gel was lightly rinsed with deionized water before being eluted with 1M nitric acid over two days. Chemical analysis of the eluent was done by the Analytical Services Group at CANMET-MMSL.

Following analysis of the DGT eluent the concentration of labile metal/metalloids was back calculated using two equations stemming from Fick's first law of diffusion as applied to a binding layer and diffusive gel as describe below.

$$M = C_e(V_{HNO3} + V_{gel})/f_e$$

Where C_e is the concentration of metals in the eluent acid, V_{HNO3} is the volume of the acid used for the extraction, V_{gel} is the volume of the resin gel and f_e in the elution factor.

$$C_{DGT} = M\Delta g/(DtA)$$

Where C_{DGT} is the concentration in the solution, M is the mass of analyte in the resin gel, Δg is the thickness of the diffusion gel and filter membrane, D is the diffusion coefficient, t is the deployment time and A is the exposure area.

	As	Co	Cr	Cu	Mn	Pb	Zn
Diffusion Coefficient (E-6 cm^2/sec)	4.95	5.94	5.05	6.23	5.85	8.03	6.08

Table 3-1: The diffusion coefficients used for calculation of the DGT concentrations. Diffusion cofficients for cations were measured at 25°C in polyacrylamide gel (Zhang & Davison, 1995). Arsenic diffusion coefficient used was for As(V) in a diffusive polyacrylamide gel at pH 4.9, 24.5°C (Panther, 2008). Speciation measurements revealed As speciation was predominantly As(V) (>99%).

3.4.5 Statistical Analysis

Toxicity test results are presented in the form of "mean ± standard deviation" for three endpoints: mortality, tissue As concentration, and dry tissue mass. These tests were conducted in triplicate (for fathead minnows) and quadruplicate (for chironomids). Comparison of means across the different treatment groups is not trivial, visual analysis of data is rarely sufficient for comparison of data. Analysis is required to determine if differences in measurements are statistically significant.

Two averages can be determined and considered statistically "different" or "the same" depending on the distribution and variance of the constituent data points. One-way analysis of variance (ANOVA) can be used to compare means of two or more samples using the F distribution (a probability distribution). The ANOVA tests the null hypothesis "samples in two or more groups are drawn from populations with the same mean values" with a rejection of the null hypothesis conclusively showing that two mean values are statistically different. For ANOVA to be reliable the data upon which it will be used must meet several requirements: (1) the data must be normally distributed, (2) the population variance between populations must be equal and (3) samples must be independent, and responses for a group are independent and identically distributed normal random variables.

The Shapiro-Wilk test was used to assess normality of the data. It tests the null hypotheses "that samples came from a normally distributed population." If the null hypothesis is rejected there are several ways to address the violation of normality. The data can be transformed using log(x) (or arcsin(x) on percentage data) are both common methods of transforming data that do not meet normality requirements. Homogeneity of variances can be tested using Levene's Test. It tests the null hypotheses that "the population variances are equal". If the variance is not homogenous a modified version of ANOVA can be used instead.

3.4.6 Methods Summary

Water and sediments were collected from sites with known historical As contamination. Sites were selected with the hope of sampling a wide variety of As host phases. Sediments were collected as a grab samples. Grid-based sampling was inappropriate for the amount of sediment required to conduct the toxicity tests (several kilograms). Water for use in the toxicity tests was collected from Yellowknife Bay (Part of Great Slave Lake).

Sediments were characterized by ESEM and synchrotron based methods in order to identify the primary As hosts. The majority of analyses were conducted in a grain-by-grain process. ESEM analysis was used to identify grains with elevated As concentration for further synchrotron analysis. At the synchrotron μXRF was used to confirm the grain identity and create element correlation maps. μXANES was used to determine As oxidation state, and μXRD was used to confirm the mineral phase. Some bulk analysis was done using sequential extractions and bulk XANES in order to determine the relative proportions of the As hosts identified during micro-analysis.

Toxicity tests were conducted were conducted in order to directly measure the toxicity caused by As contamination at each site. Toxicity tests were conducted with *Pimephales promelas* (fathead minnows) and *Chironomus dilutus* (a non-biting midge). The fathead minnow tests were conducted in a conical test chamber meant to better simulate a water column. The chironomid tests were conducted in normally shaped beakers.

The geochemical conditions within the toxicity tests were measured by mini-peeper, DGT and grab sample in order to directly analyze the test exposure conditions. Metal/metalloid concentration, As speciation, DOC, O_2, and pH were measured during the tests. These measurements were also conducted to allow for the correlation of the solid phase As hosting and the toxicity test results.

3.5 Results

3.5.1.1 Water and Sediment Concentrations

Surface and pore-waters at Giant Mine were dominated by the major anions SO_4^{-2}, NO_3^-, Cl^-, and cations Ca^{+2}, Mg^{+2}, Na^+, and K^+ (Table 3-2).

	SO_4^{-2} (meq)	NO_3^- (meq)	Cl^- (meq)	Ca^{+2} (meq)	Mg^{+2} (meq)	Na^+ (meq)	K^+ (meq)
YKBEACH-SW	0.11	>0.0010	0.10	0.46	0.25	0.12	0.03
BPOND-SW	7.27	0.0306	4.01	7.01	2.69	2.34	0.11
BOVEG-SW	9.24	0.0356	4.96	8.67	3.32	2.97	0.13
YKBEACH-PW	1.69	>0.0010	0.62	4.67	3.21	1.16	0.17
BPOND-PW	5.48	>0.0010	3.22	6.85	3.43	1.39	0.24
BOVEG-PW	5.62	0.2097	2.26	7.75	3.07	1.58	0.14

Table 3-2: The pore-water (pw) and surface water (sw) concentrations of the major anions, cations and trace metalloids measured at Giant Mine. Quality assurance replicates are reported in the appendices.

Several field parameters were measured and found to vary consistently between surface and pore-water. pH of pore-water was consistently higher than the corresponding surface water, and alkalinity was also higher in pore-water. Redox potential varied only slightly between sampling sites and within sites between surface and pore-water.

	Temp (°C)	pH	pE (V)	Cond (µs/cm)	DO (mg/L)	TDS (g/L)	Alkalinity (mg/L $CaCO_3$)
YKB-SW	25.1	8.11	2.43	101	8.81	0.07	26.9
BVEG-SW	19.8	7.02	1.39	1551	7.58	1.19	55
BPOND-SW	21.9	7.97	1.93	1335	9.46	0.92	55.3
YKB-PW	21.7	6.98	0.90	933	3.47	0.65	324
BVEG-PW	18.8	5.65	0.72	1267	4.15	5.65	275.2
BPOND-PW	23.1	6.48	N/A	1299	5.82	0.874	173.4

Table 3-3: The field parameters measured prior to disturbing the waters with sediment sample collections. Baker Pond pE is not included due to probe malfunction during collection.

Arsenic concentration in the measured sediments ranges from 39 ppm to 17200 ppm (site averages are presented in Table 3-4). None of the sediments have concentrations below the CCME interim sediment quality guideline of 5.9 ppm for the protection of aquatic life in freshwater systems (Canadian Council of Ministers of the Environment, 1999). For full analytical results see Appendix A and B.

After manual mixing the sediments were subsampled in triplicate to assess their homogeneity. The relative standard deviation of the As concentrations for the three sites indicate varying degrees of heterogeneity.

Site	Sediment (ug/g)	Relative Standard Deviation (n=3)
YKBAY	42.5	9%
BVEG	3012.3	38%
BPOND	14133.3	19%

Table 3-4: The average As concentration and relative standard deviation of the sampled sediments which were separated into triplicates after manual mixing.

The relative standard deviation (RSD) of the As concentration reveals that the sediments are highly heterogeneous with respect to As concentration. The complicated history of deposition and contamination at these sites has provided low volume, high concentration As-hosts that are rare and not evenly distributed.

The sediment with the most variable As content comes from Baker Outlet Vegetated Area and had significant mass of roots present in the sediments. The root and vegetation content of these sediments likely contributed to the high As variability by diluting the sediments by an amount proportional to their mass. Proper homogenization of the BVEG sediments would require breaking the roots and vegetation into small enough pieces that they could be evenly distributed among subsamples.

All sampling sites were near previously studied locations. YKB sediments are much lower in As in sediment and pore-water than the sediments measured by Andrade (2006) who sampled fully submerged sediments further from the shore at 1.5m water depth. Baker Outlet sediment As concentration is consistent with those measured by Fawcett (2009), though the pore-water concentrations recorded previously in the nearby location are much lower than those recorded during this projects sampling. In all sites As(V) was dominant in surface water and As(III) was dominant in pore-water (Andrade, 2006,Fawcett, 2009).

Arsenic in sediment pore water also varied widely between the sample sites. Concentrations of As varied from 0.098 ppm to 0.28 ppm in surface water and from 7.5 ppm to 220.1 ppm in pore water. All measurements were above the CCME water quality guideline for the protection of freshwater aquatic life

of 0.005 ppm. Arsenic concentration is ordered by YKBAY<BVEG<BPOND, a trend that holds for As in the sediment, surface water, and pore water concentrations.

	Sediment (ug/g)	Surface Water As(aq) ppm	Pore-Water As(aq) ppm
YKBAY	43±4	0.098±0.003	7.45±0.02
BVEG	3000±1000	0.135±0.001	11.0±0.1
BPOND	14000±3000	0.282±0.002	221±1

Table 3-5: Average bulk As concentrations of the sampled sediments and the waters that they were exposed to (n=3). Measurement precision was determined by standard deviation of the triplicate measurements and varies for each site.

For full analytical pore-water results see Appendix B.

3.5.2 Arsenic Speciation in Water and Sediments

3.5.2.1 Aqueous Arsenic Preservation

Three methods of As preservation were tested: cooling to 4°C, freezing at -4°C, and cooling to 4°C with HCl acidification to pH 2. The preservation methods were judged based on the agreement of the sum of speciation measurements (As(III) + As(V)) with As(T) (measured by ICP-MS with metal concentrations), as well as on the relative standard deviation of the measurements that were taken in triplicate for Baker Vegetated surface water. All speciation measurements were lower than the As(T) that was measured separately, implying that some As was lost during column separation, transformation into organic As, or precipitation (despite not being observed) prior to measurement.

	No Preservation	Freezing	HCl Acidification
% Diff	-37.6%	-33.6%	-17.9%
% Std Dev	6.4%	1.5%	3.1%

Table 3-6: The variability in aqueous As speciation measurements for each of the tested methods. Methods were judged based on the agreement of sum of the As(III) and As(V) with As (T) which was measured on separate samples that were collected at the same time and measured by ICP-MS with other total metal concentrations. No visible precipitation was observed in any of the samples. n=3.

Sulfate concentrations were a maximum of 444ppm in BVEG surface water. No visible precipitation reactions occurred in the samples. Other researchers have only observed sulfate/As precipitations at considerably higher concentrations such as 1290ppmsulfate and 1.8ppm As . As a result As-S phases are unlikely to have precipitated, even at low levels.

The freezing method had the greatest precision (1.5% RSD) and the acidification method was slightly less precise (3.1% RSD). Acidification had best accuracy with the As(T) data (-17.9%) with the freezing method having only half (-33.6%) that accuracy. The cooling only method had the worst agreement with As(T) (-37.6%) values and was also the least precise (6.4% RSD). Conventional acid preservation was determined to be the most accurate method of As speciation preservation because it most closely agreed with As(T) values. Since precipitation of As-S phases, which was the primary concern with traditional acidification, was not observed, it is not surprising that traditional acidification was found to be the best method.

	Surface Water			Pore Water		
	YKBAY	BOVEG	BPOND	YKBAY	BOVEG	BPOND
As(III) (ppb)	< 7.7	< 7.9	10	6624	8637	185400
As(V) (ppb)	76	96	235	130	1767	10180

Table 3-7: Arsenic speciation measurements when preserved by acidification to pH 2 with HCl (n=1).

The surface water measured at the three sites was in all cases predominantly oxidized with only BPOND having a measurable fraction of As(III).

The As(III)/As(V) ratios observed were not consistent with theoretical equilibrium values calculated by PHREEQC (minteq database) based on measured Eh. Similar disequilibria of As(III)/As(V) in surface and pore water is well documented in natural and mining impacted systems (Bodénan *et al.*, 2004). In all cases the As was more reduced than the predicted values and with the trend of disequilibrium following YKBAY>BPOND>BOVEG.

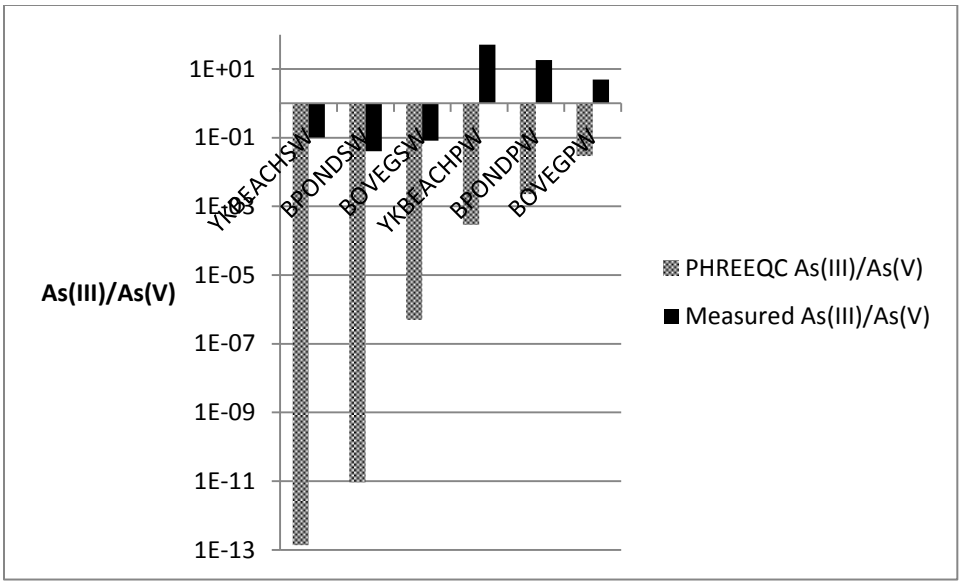


Figure 3-11: Arsenic speciation values and predicted speciation values based on Eh/pH values. PHREEQC ratios were calculated using Eh values and measured ratios are calculated from Table 3-7.

The observed As speciation trend where As(III) is dominant in pore-water and As(V) is dominant in surface water is consistent with BPOND and BVEG data from a previous study (Fawcett, 2009). Additional As pore-water speciation data is not available for YKB sediments.

3.5.3 Arsenic Hosts

Using the synchrotron and ESEM based techniques outlines in section 3.2 several As hosts were identified. Table 3-8 lists the all discrete As hosts that were identified or suspected to exist but not identified (As sulphides) in the sampled sediments.

	Yellowknife Bay	Baker Outlet Vegetated Area	Baker Pond
Arsenic Trioxide		Found	Found
Iron Oxide		Found	Found
Arsenopyrite		Found	Found
Scorodite		Found[1]	
As sulfide			
Root Plaque		Found[2]	

Table 3-8: The As hosts identified by synchrotron and ESEM analysis in the three sample sites.[1] Found rimming arsenopyrite. [2] Found on Cattail roots.

3.5.3.1 Arsenic trioxide

As_2O_3 was identified as one of the As hosts in Baker Pond and Baker Creek Outlet sediment thin sections. ESEM analysis was the principle tool used to identify As_2O_3 because it occurs as a distinctly bright phase under the BSE detector (Figure 3-12). The ESEM beam noticeably damaged the As_2O_3 grains in all cases. Wrye (2008) postulated that the ESEM beam may cause As_2O_3 to melt and recrystallize, but showed that it did not change its oxidation state or mineral form. While synchrotron-based μXRD was used to confirm that As_2O_3 is present as arsenolite (instead of the polymorph claudetite), the identified phase is referred to as As_2O_3 due to its anthropogenic origins. Specifically, arsenolite forms naturally by the oxidation of arsenopyrite, realgar and native As in reducing conditions (Nordstrom and Archer, 2003) while As_2O_3 has a synthetic origin.

Most of the As_2O_3 grains appeared to have a smooth texture under ESEM analysis with the BSE detector though some samples have a more mottled appearance. There were no observed reaction rims. The energy-dispersive X-ray spectroscopy (EDX) spectrum revealed As as the only element with non-trace concentrations that could not be associated the slide mount (Si).

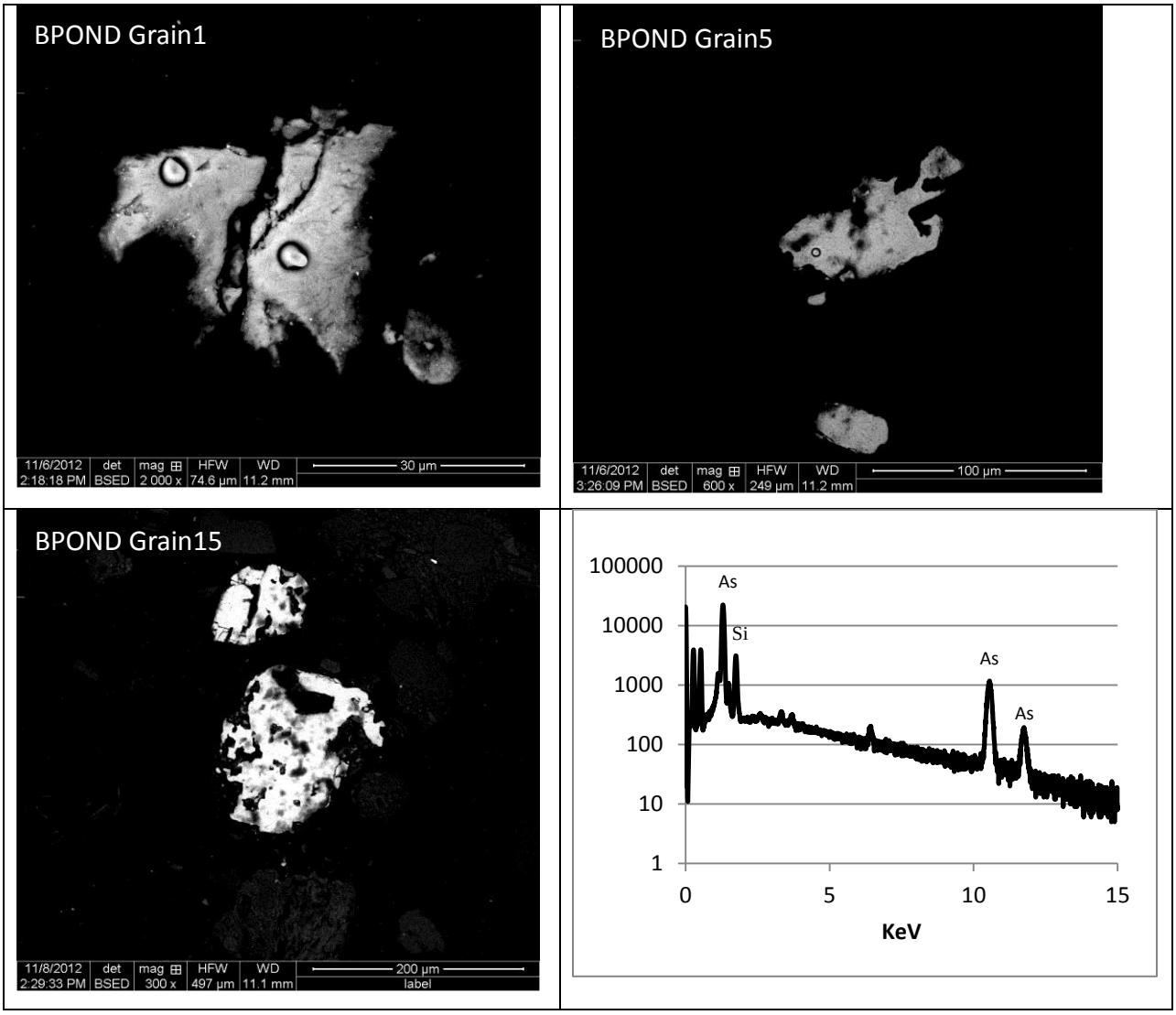


Figure 3-12: Three As_2O_3 grains identified by backscatter detection on ESEM and the characteristic EDS spectrum observed for all three grains.

After identification of As_2O_3 grains was achieved on the ESEM at Queen's University the locations were recorded for confirmation analysis using µXRD synchrotron techniques.

Targeted grains were re-identified using Fly-Scan elemental mapping at the synchrotron light-source. Grains were then subjected to µXRD and processed to find a matching diffraction pattern. As_2O_3 did not diffract smoothly, instead producing irregular spots in the 2D XRD images. This occurs when the crystal size of a mineral is large relative to the size of the synchrotron beam. The orientation of the crystal

grains also influences the spotty rings (Walker, 2005). Grains were also subjected to μXANES for additional confirmation, but self-absorption was prohibitive in obtaining usable spectra.

Grains are consistent with those found by previous sampling and ESEM analysis of Giant Mine soils. Bromstad (2011) identified As_2O_3 in Giant Mine soils. These grains have identical 2D μXRD images and similar smooth and mottled textures though no reaction rims were observed in this test's sediment As_2O_3.

Arsenic trioxide was only found in Baker Pond and the Baker Outlet Vegetated area. As_2O_3 was the most abundant in Baker Pond. MLA (mineral liberation analysis) was required to search a BVEG thin section to find the mineral. Of 267,555 identified grains (a low count due to tightly packed grains not resolving) in the sample 9 were As_2O_3.

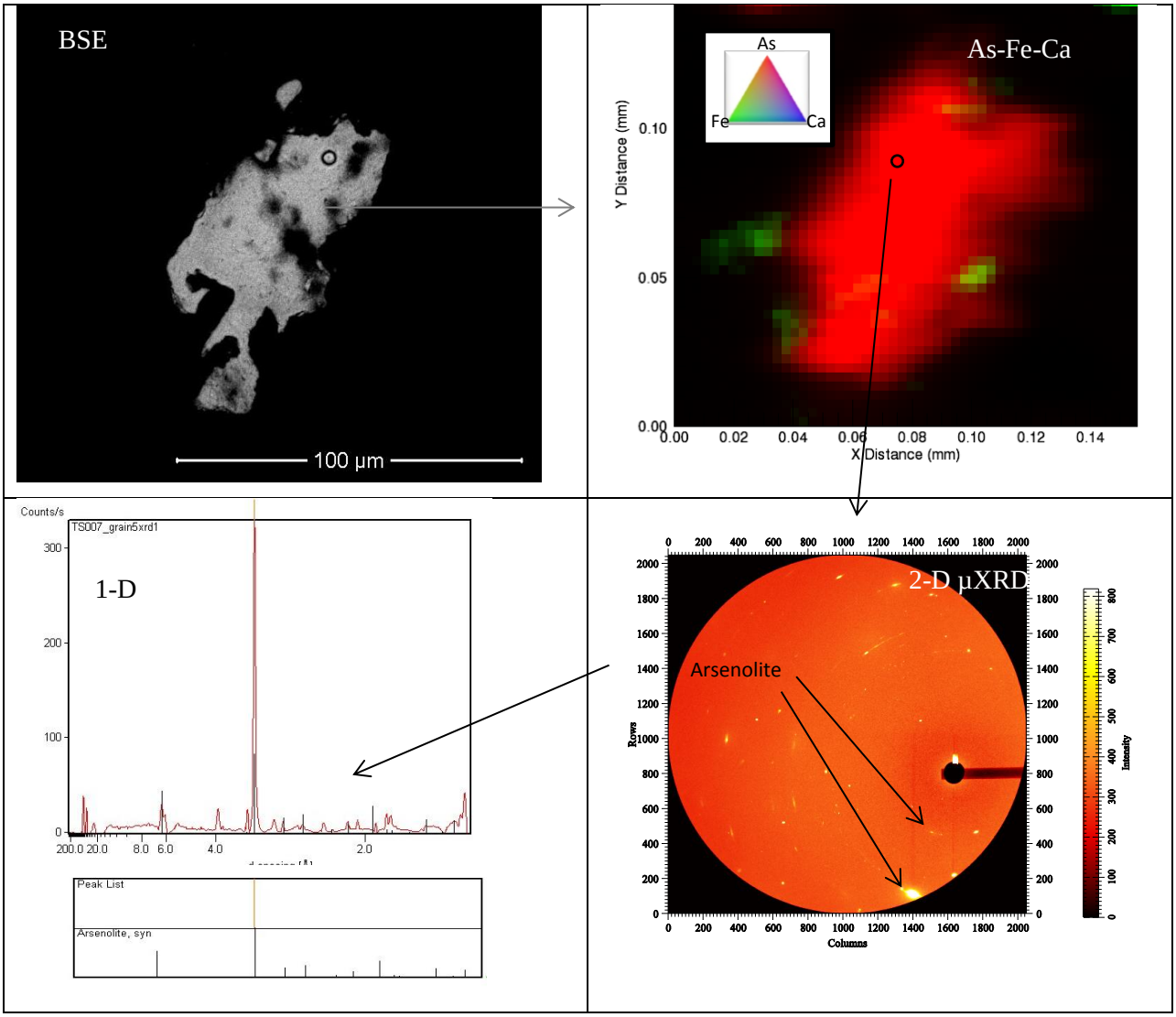


Figure 3-13: As_2O_3 identification of TS007_GRAIN5. Clockwise from the top left: BSE photo from an ESEM, an µXRF flyscan map, a µXRD taken from the indicated locations, and a 1D reduction of the µXRD that was used to identify the grain as arsenolite.

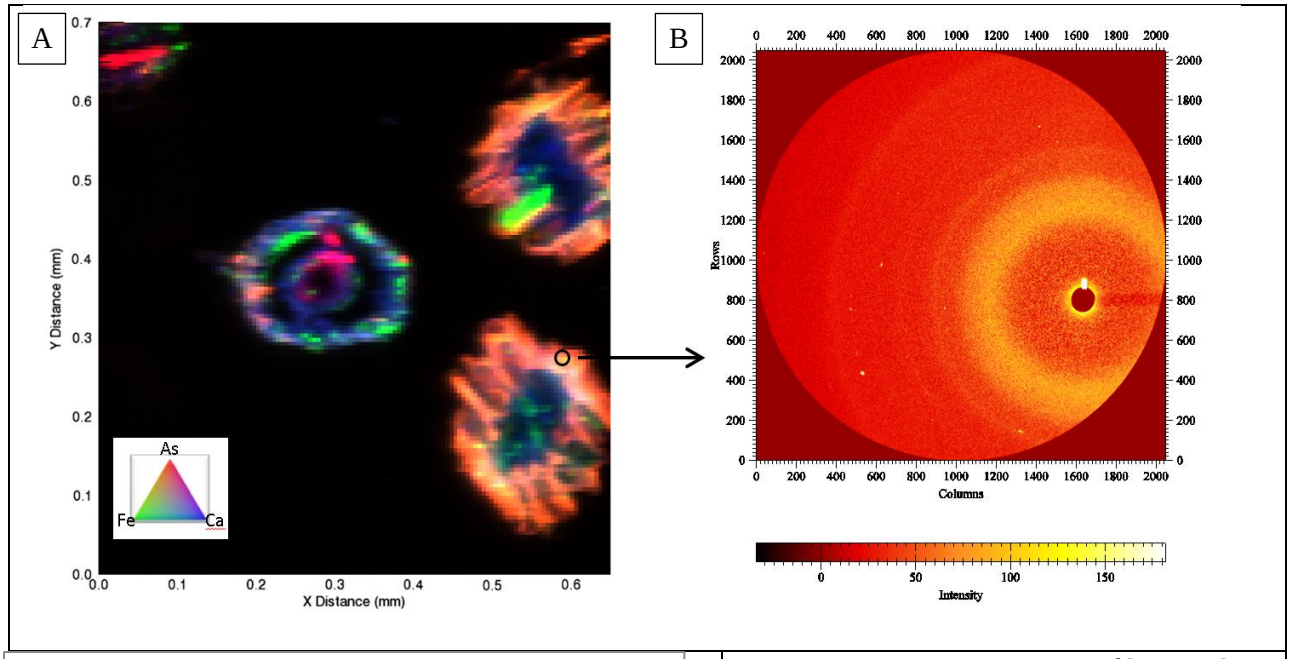
3.5.3.2 Plant Roots and Vegetation

Arsenic in the Baker Outlet Vegetated area is contained in iron rich vegetation root plaque. The cross section RGB element mapping in Figure 10 shows overlap of As and Fe within orange areas. Plaque containing both As and Fe correlation occurs on the vegetation rims. Although As counts were too low for detection on the Queen's ESEM, synchrotron µXRF mapping was used to detect and analyze the As rich root rims.

The As and Fe correlation can be directly seen in the element correlation plot Figure 3-14C. The sharp line on the As/Fe border illustrates that the Fe concentration of the roots controls the As concentration. Once As has occupied all available Fe adsorption sites the highest available As:Fe molar ratio is achieved and seen along the sharp boundary. Lower As:Fe ratios can be observed in the correlation plot, indicating that As is not a controlling element because Fe can exist in high concentration without the presence of As, but not vice versa.

The As rich rim was analyzed by μXRD numerous times but no appreciable diffraction was observed. μXANES was conducted and revealed that the majority was As(V) at 88% with some As (III) at 12%. The results are consistent with an amorphous iron oxide root plaque that adsorbed dissolved As as characterized by (Blute *et al.*, 2004)) who used micro-tomography techniques to measure that adsorbed As in a similar Cattail root system was 20% As(III) and 80% (V).

In the upper left corner of the μXRF map a high As, low Fe, oblong grain was observed. This unknown As host was not noticed until after analysis at the synchrotron ended and was unfortunately not investigated further. It appears in Figure 3-14C as the high As/ no Fe line.



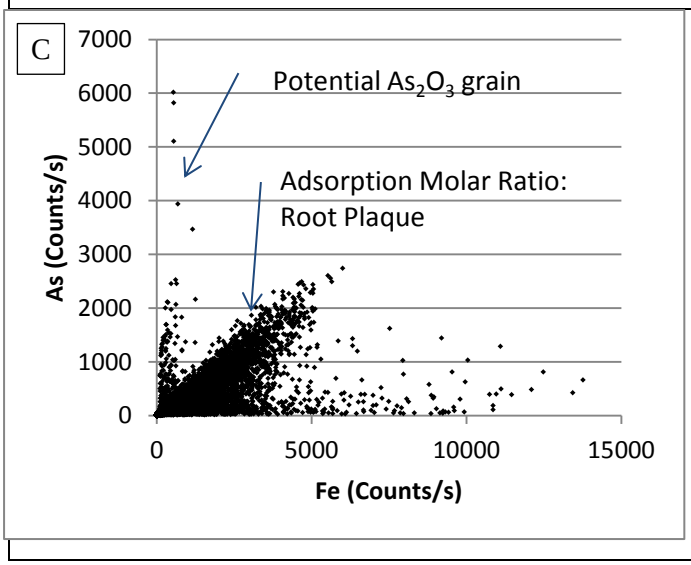


Figure A: µXRF cross section of horsetail root TS002_Root1 collected from Baker pond illustrating the As and Fe overlap on vegetation rims. B: µXRF showing negligible defraction, illustrating the amorphous nature of the As and Fe. C: An element correlation plot of As and Fe, illustrating the correlation between the elements.

Figure 3-14: Iron root plaque identification on TS002_Root1. A: µXRF fly-scan element map. B: µXRD taken from the indicated location. C: As-Fe element correlation plot from the same point.

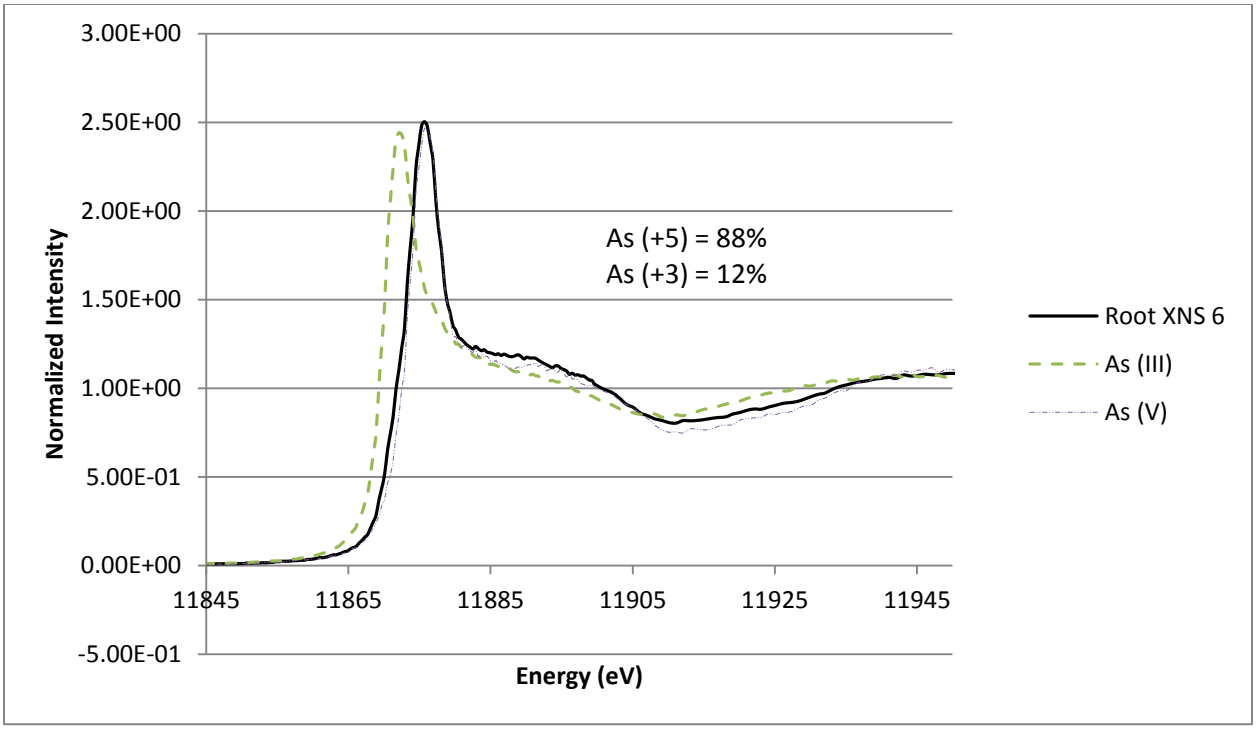


Figure 3-15: µXANES spectra of the oxidation state of the As sorbed to amorphous iron rimming the horsetail roots of Baker Vegetated compared to lab standards. Arsenolite and scorodite were used as the As(III) and As(V) standards.

3.5.3.3 Arsenopyrite

Arsenopyrite was present in both Baker Pond and Baker Outlet sediments. Arsenopyrite was identified using the same ESEM and synchrotron techniques as discussed previously. The subhedral smooth texture and shape allowed for easy preliminary identification of arsenopyrite targets on the ESEM. For the arsenopyrite identified below µXRD revealed a scorodite pattern alongside the arsenopyrite pattern, suggesting some transformation of the primary arsenopyrite.

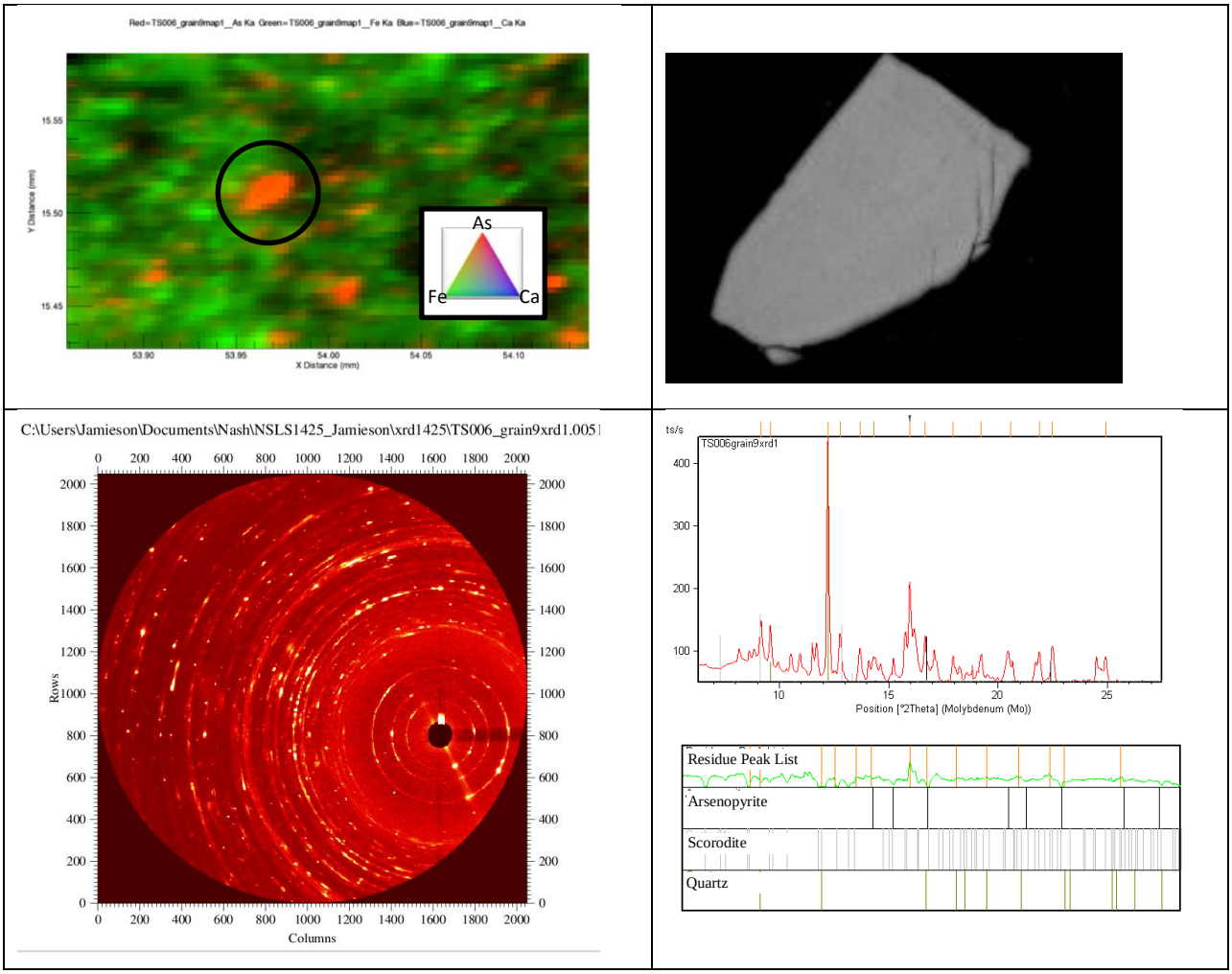


Figure 3-16: Arsenopyrite identification of grain TS006_GRAIN9 from BVEG. Clockwise from the top left: µXRF flyscan map, BSE photo from an ESEM, a 1D reduction of the µXRD, and the µXRD taken from the rim.

3.5.4 Whole Sediment Arsenic Host Tests

The BCR three step leach test was conducted to estimate the As speciation in the sediments. The three leachates correspond to (1) exchangeable/acid-extractable metals and metalloids (2) metals and metalloids associated with reducible phases and (3) metals and metalloids released by oxidation. This procedure has been widely used and documented for many matrices, including sediments (Baig *et al.*, 2009). Sequential extraction of the bulk sediments was undertaken to generate bulk As speciation data to

allow for comparison to bulk XANES data for the same samples. All extractions were conducted in triplicate. Full results are available in Appendix H.

The certified reference material BCR-701 was processed alongside the sample sediments for quality assurance purposes. BCR-701 is not certified for As concentration but comparisons can be made to the other trace elements that were analyzed. The BCR-701 extraction shows good agreement with certified values for steps 1 and 3 and there was some significant variation in the 2nd step. Nickel measurements illustrate this trend in Table 3-9.

	Step 1	Step 2	Step 3
Ni BCR- 701 Measured Value (mg/kg)	17.7	26.6	15.3
Ni BCR-701 Accepted Value (mg/kg)	15.4	15.02	16.2

Table 3-9: The measured and accepted Ni values for the BCR-701 standard. This trend persisted in all measured elements.

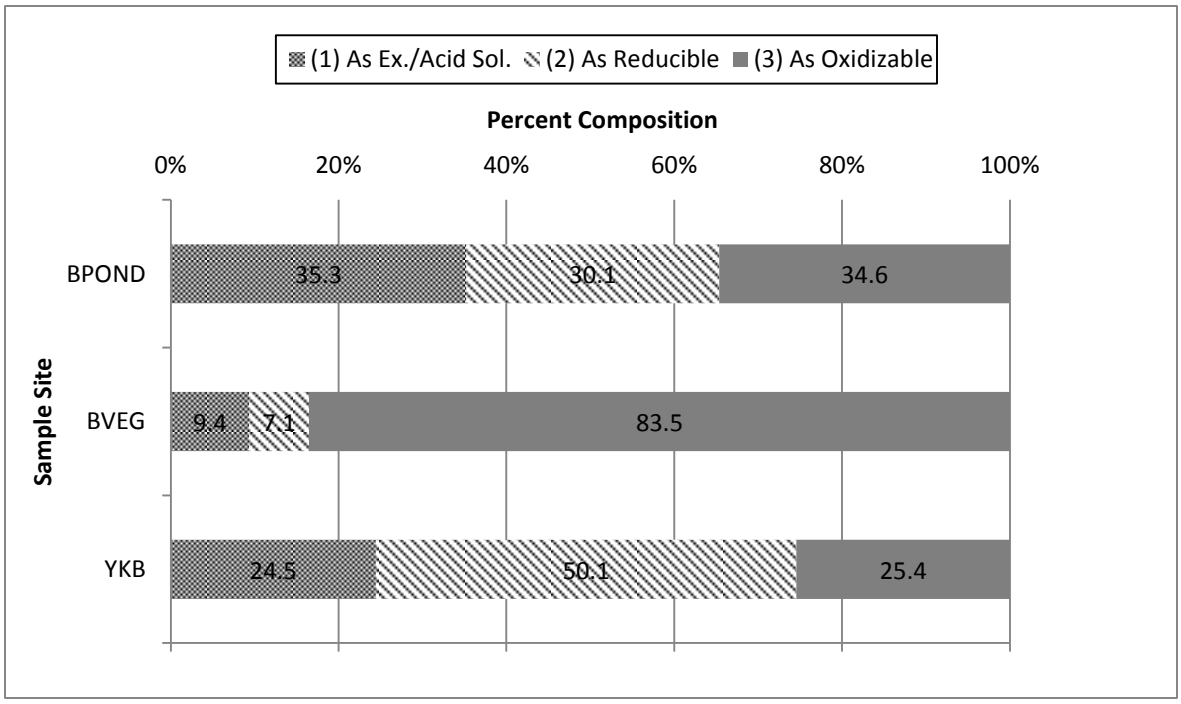


Figure 3-17: BCR sequential extraction As results for the sampled sediments. Values are average of triplicate measurements (n=3).

Sample Site	SSE As (ug/g)	Sediment As (ug/g)	SSE Extraction %
YKB	18.1±1.3	42.5±3.8	43%
BVEG	2490.3±950	3000±1200	82%
BPON	10600.7±9500	14100±2700	75%

Table 3-10: Comparison of total sum of As extracted during the sequential extractions "SSE As" and the whole sediment concentration as determined by *aqua regia* digestion "Sediment As" where "SSE Extraction %" is the ratio between the two. Measurement precision was determined by standard deviation of the triplicate measurements and varies for each site.

Bulk XANES was undertaken at beamline X-11 at the NSLS for the purpose of determining bulk As oxidation state to expand on the interpretation of the As-hosting made from the sequential extraction and grain-by grain analysis.

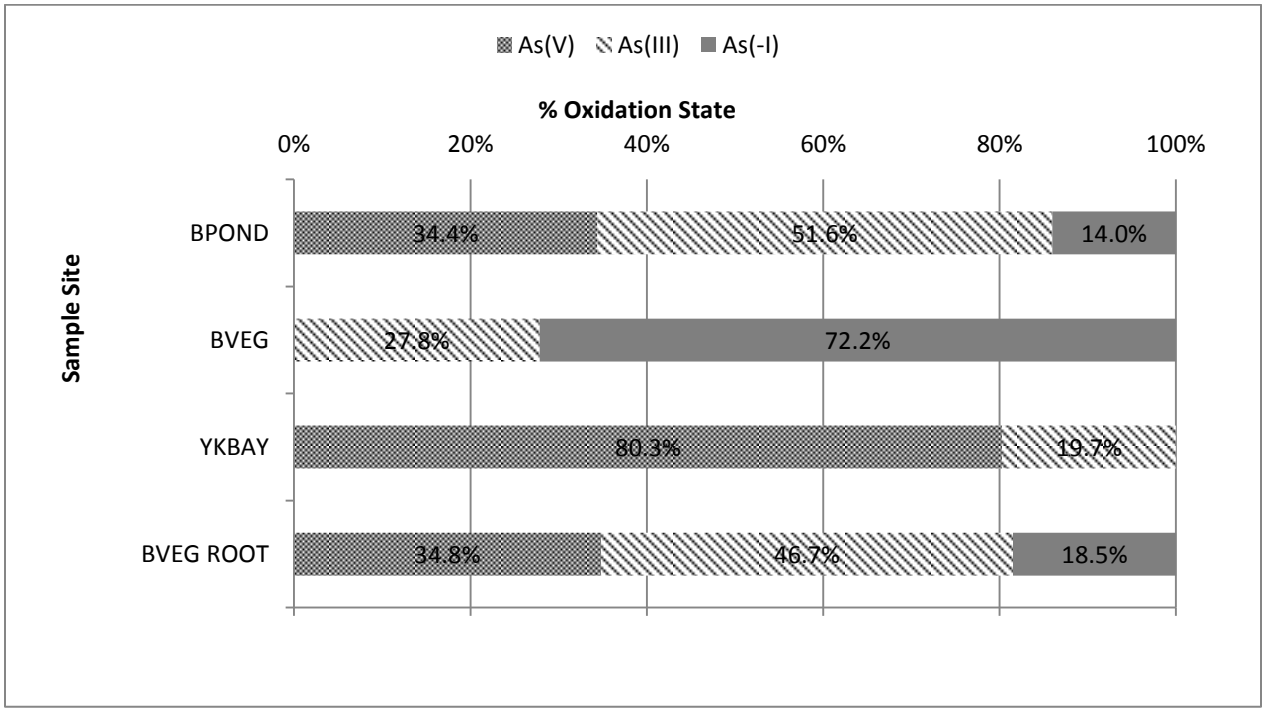


Figure 3-18. Bulk XANES spectra showing the average oxidation state of the sampled sediments and the roots from Baker Outlet Vegetated area. n=3 for the sediments and n=1 for the roots. Measurement precision was determined by standard deviation of the triplicate measurements and varies for each site, where appropriate.

	As(V)	As(III)	As(-I)
BVEG ROOT	34.8%	46.7%	18.5%
YKBAY	80.3±0.2%	19.7%±0.2%	0%±0%
BVEG	0%±0%	27.8±2.43%	72.2%±2.43%
BPOND	34.4%±3.5%	51.6%±2.57%	14.0%±3.8%

Table 3-11: Arsenic Bulk XANES oxidation state for the three sites and the roots found in BVEG. n=3 for the sediments and n=1 for the roots.

3.5.4.1 Bulk Phases: BPOND

Baker Pond's complex depositional history and As contamination is represented by presence of the As in each sequential extraction phase and the presence of all three oxidation states in the bulk XANES spectrum. Arsenic was directly observed in As_2O_3 (As III), arsenopyrite (As –I) synchrotron analysis and Fe-oxides (As III and V) grains during ESEM analysis. The bulk XANES oxidation measurements suggest that As_2O_3 and Fe-oxides are the most prevalent hosts for As at Baker Pond. Realgar (As_4S_4) exists as As(II)and was searched for by MLA on the ESEM and was not found.

3.5.4.2 Bulk Phases: Baker Outlet Vegetated

Arsenic in BVEG sediment is the most reduced of the three sites with over 72% of the As in the –I state. This corresponds to the sequential extraction data which shows that the majority of the As (83.5%) is found in the oxidizable phase. Both of these statistics suggest that most of the As is found in arsenopyrite (As -I) which can undergo oxidative-dissolution.

$$4FeAsS + 11O_2 + 6H_2O = 4Fe^{2+} + 4H_3AsO_3 + 4SO_4^{2-}$$

A single grain of arsenopyrite (As -I) was observed with scorodite rimming (As V)The bulk XANES analyses of the roots from BVEG reveal that root As is primarily in the III and V state, which is consistent with As adsorbed to iron oxides. The presence of As(V) in the roots and absence in the sediments suggests that the roots are only a minor host for As in the BVEG system.

3.5.4.3 Bulk Phases: Yellowknife Bay

Yellowknife Bay sediments contain relatively low total As concentrations at 42.5 ppb. The As was poorly extracted by the SSE test (43%), which reveals that the As and less labile than the other sites

(82% and 75% extraction). The As is primarily As(V) with some As(III). The As is found in all three SSE extraction phases, suggesting that the element is found in a variety of minerals at low concentration. Previous research on sediments deeper than YKB sampling site has identified roaster-generated Fe-oxides (As III and V) (Andrade, 2006) and arsenopyrite (As -I) from tailings is consistent with the depositional history of this site. Realgar (As_2S_2) exists as As(II)and was searched for by MLA on the ESEM and was not found.

3.5.5 Toxicity Tests

Sediment toxicity was evaluated through the endpoints: mortality, dry tissue mass, and tissue As concentration. *Pimephales promelas* tests were performed in triplicate and *Chironomus dilutus* tests were performed in quadruplicate. The *Chironomus dilutes* tests had an additional replicate in order to test the assumption that the mini-peepers in the test beakers were not influencing the test. This assumption appears to have been validated based on qualitative observation of the data.

Statistical Package for the Social Sciences (SPSS) was used for statistical analysis of the three endpoints to determine which results were statistically relevant. Several different statistical tests were used depending on whether or not the data was normally distributed and had homoscedasticity. BPOND was excluded from analysis of all data sets because it skewed the rest of the data by removing its "homogeneity of variances" and normalized distribution, making further analysis require less powerful statistical tests. BPOND is obviously quantitatively different from the other sites. 100% mortality does not require further analysis to justify this conclusion.

Surface water from Yellowknife Bay was collected off-shore of the Giant Mine town site and used for the toxicity tests. Water chemistry was sent for analysis with other surface and pore-water samples. All major cation and anion concentrations were below detection limits, only As (9 ppb) and Cr (1.24 ppb) were quantified for these waters. The control water was not re-analysed until it was placed in the fathead minnow toxicity tests.

	As	Co	Cr	Cu	Ni	Pb	Sb
Great Slave Lake Control Water (ppb)	18.3	< 0.1	1.1	2.0	1.2	< 0.3	1.0

Table 3-12: Trace element concentrations in the great slave lake control water used in the fathead minnow toxicity tests after 10 days in the test chambers.

The surface water was not intended to be a source of toxicity to the organisms. This assumption was tested by including two control groups. A lab water control (LS) contained laboratory grade silica sand and purified water while the reference water sample (RS) utilizes the same silica sand and lake water from Yellowknife Bay both have very similar survival levels. In all cases there were no statistically observed differences in toxicity between the control groups.

3.5.5.1 Chironomus Dilutus

3.5.5.1.1 Survival

As seen in Figure 3-19, no chironomids survived in the most As rich sediments (Baker Pond). In general, the toxicity trend follows the total As trend toxicity where BPOND>BOVEG>YKBAY. A second test using BPOND sediments diluted to 10% and 40% concentration with sterile lab sand used in the control tests was conducted. Both of these tests also caused 100% mortality in the exposed organisms.

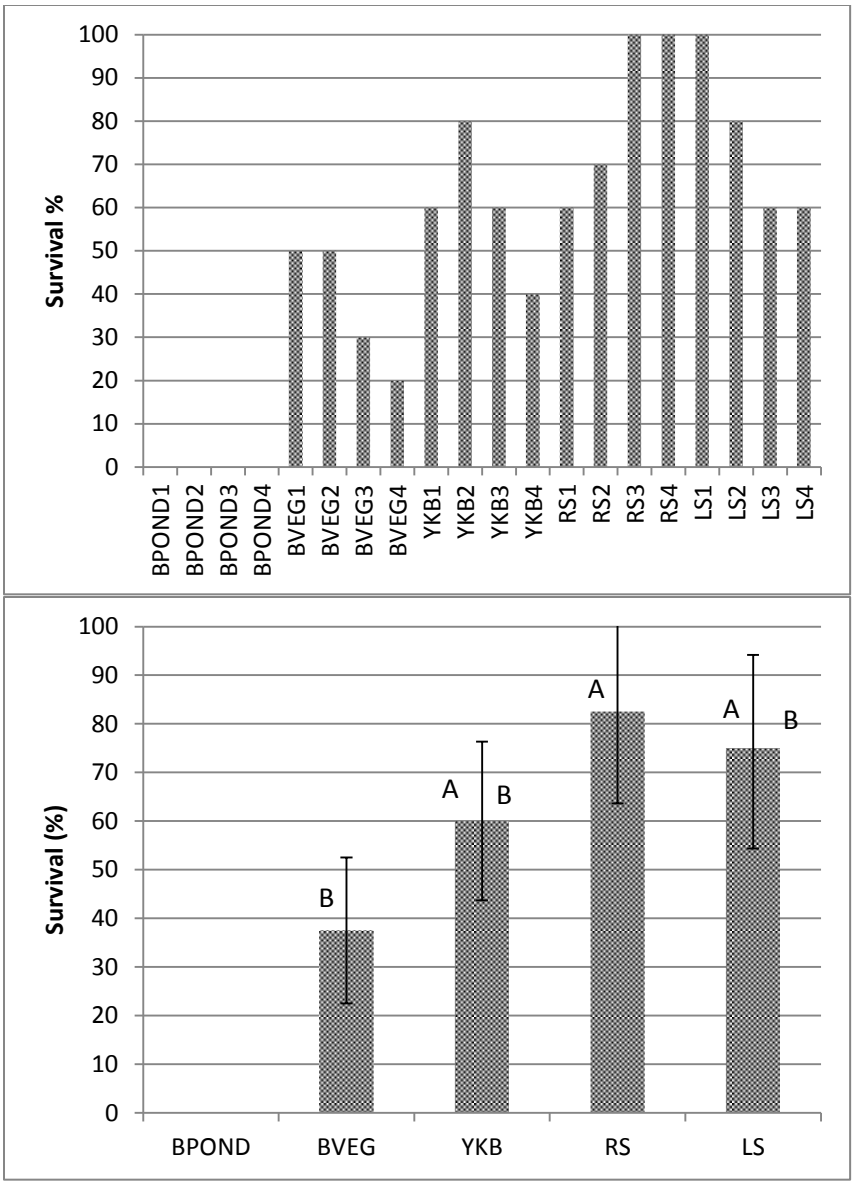


Figure 3-19: Graphs of the survival rate of the chironomid toxicity tests. The top shows survival % from each replicate and the bottom displays the averages and standard deviation. Means with the same letter are not statistically different. BPOND, BVEG, and YKB correspond to the three sample sites while RS and LS are the reference water standard and lab water standard, respectively.

A one-way ANOVA test was conducted to determine if the different sediment treatments caused statistically significant changes to the survival rate of the chironomids. The data were normally distributed for each group, as assessed by Shapiro-Wilk test ($p > .05$); and there was homogeneity of variances, as assessed by Levene's test of homogeneity of variances ($p = .562$). Data are presented as mean ± standard deviation. Survival rate was significantly different between different sediment exposures ($F(3,12)=4.909$, $p=0.019$). Survival Rate increased from the BakerPond (0±0), to Baker Outlet

(0.375±0.15), to YKBAY (0.60±0.16), to LS (0.75±0.19), to RS (0.825±0.21). Tukey post-hoc analysis revealed that the increase from BVEG to RS (.45,95%CI, 0.74 to 0.83) was statistically significant (p=0.018.

3.5.5.1.2 Tissue Mass

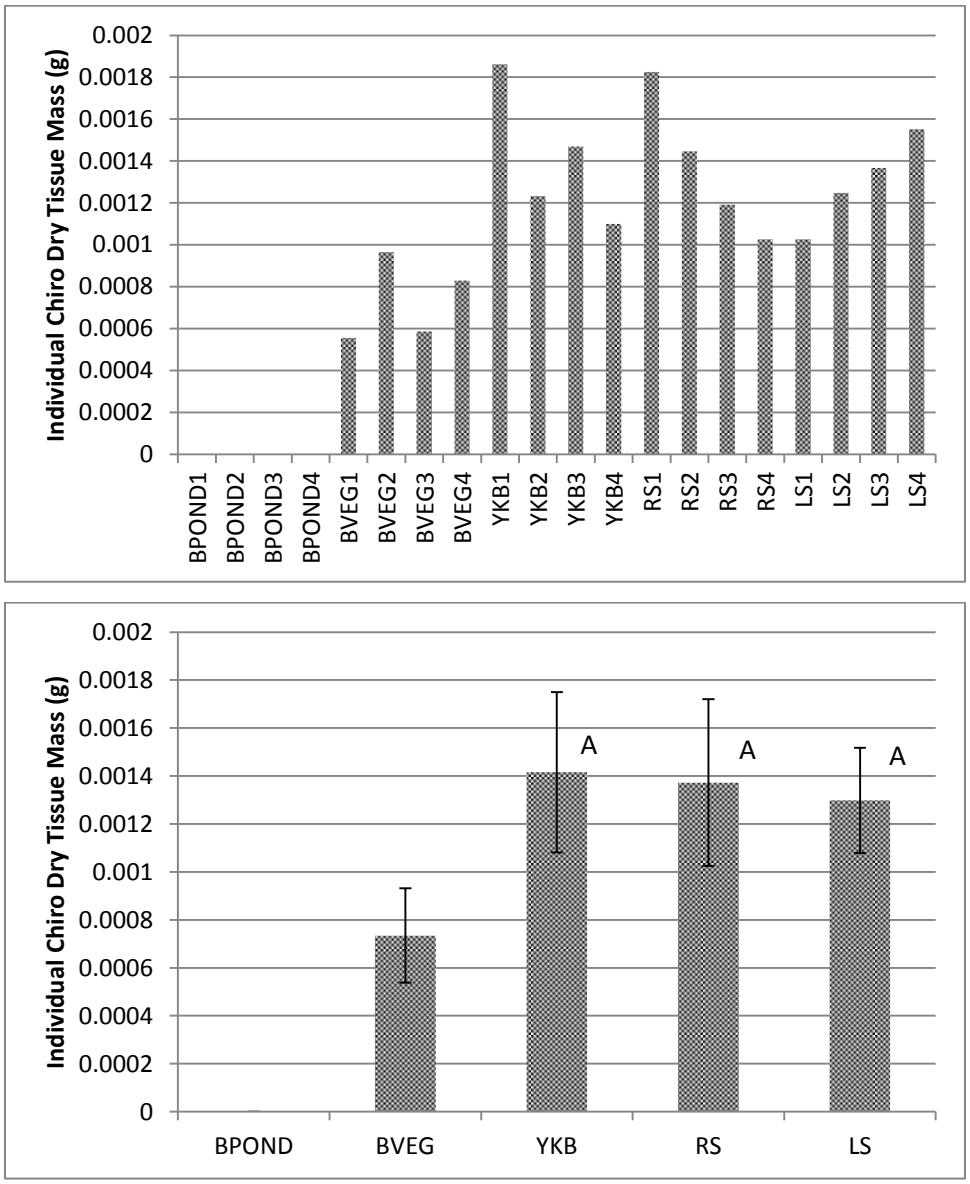
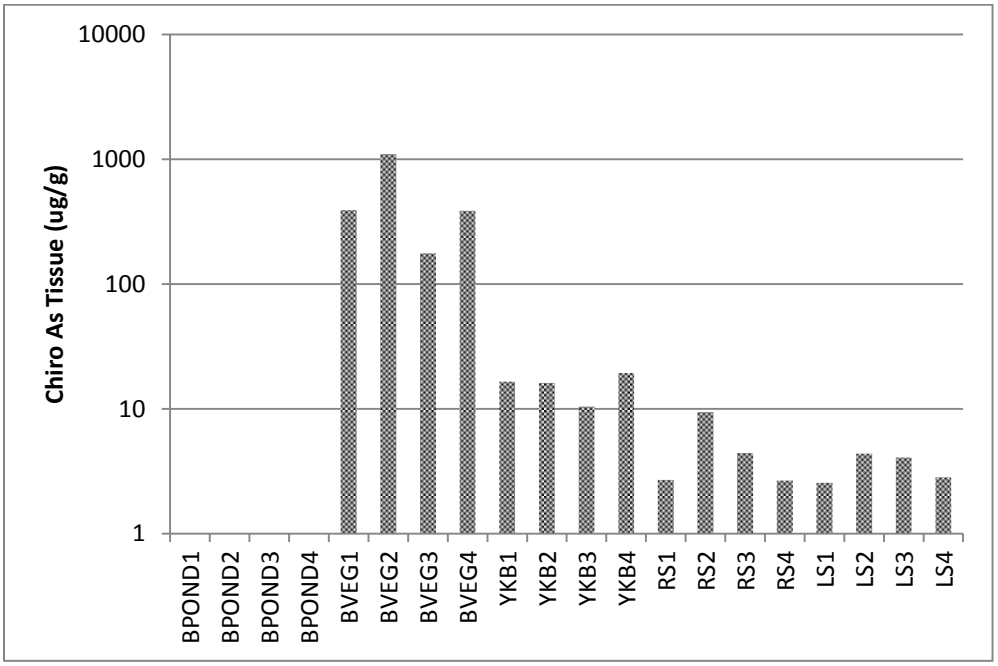


Figure 3-20: The individual dry tissue mass of the chironomids after the toxicity test. The top shows individual dry tissue mass from each replicate and the bottom displays the averages and standard deviation. Means with the same letter are not statistically different. BPOND, BVEG, and YKB correspond to the three sample sites while RS and LS are the reference water standard and lab water standard, respectively.

A one-way ANOVA test was conducted to determine if the individual tissue mass of the chironomids varied between the sediment exposure groups. The data were normally distributed for each group, as assessed by the Shapiro-Wilk test ($p > .05$): and there was homogeneity of variances, as assessed by Levene's test of hom ogeneity of variances ($p = 0.597$). Individual tissue mass was significantly different between the exposures ($F(3,12) = 5.044$), $p = 0.017$). Individual tissue mass increased from Baker Pond (0.0±0.0) to BVEG (0.007±0.0002), to LS (0.0013±0.0002), to RS (0.0014±0.0003), to YKB (0.0014±0.0003). Tukey post-hoc analysis revealed that the increase from BVEG to YKBay, 0.0007g (95%CI,0.000088 to 0.0012750) was statistically significant (p=0.023) as was the increase from BVEG to RS, 0.0006g (95%CI, -0.00055 to 0.00064) (p=0.034). Tukey post-hoc analysis calculated that the increase from BVEG to LS, 0.0006g, was not statistically significant (p=0.065), however the Games-Howell test calculated that it was (95%CI, 0.000051 to 0.001077) (p=0.034).

3.5.5.1.3 Tissue Concentration



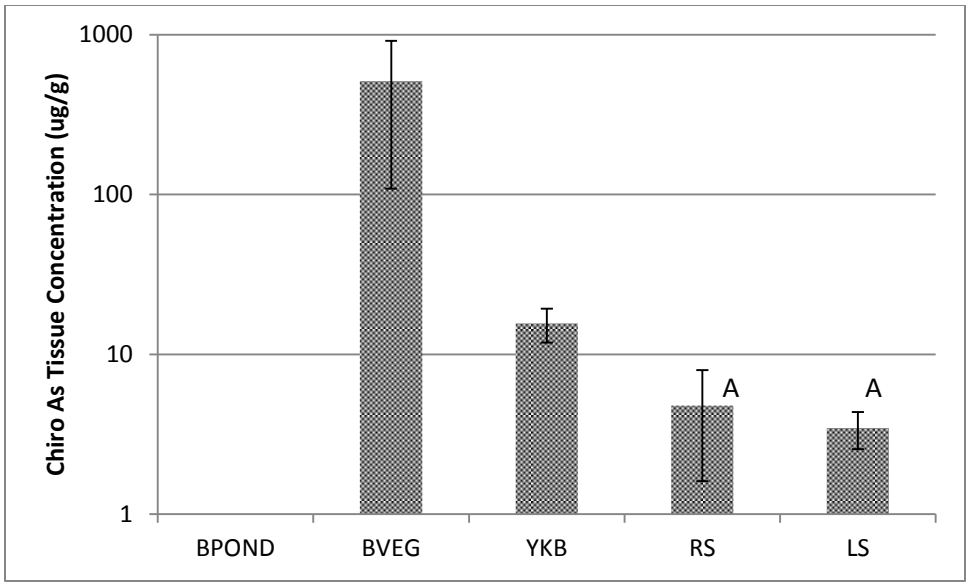


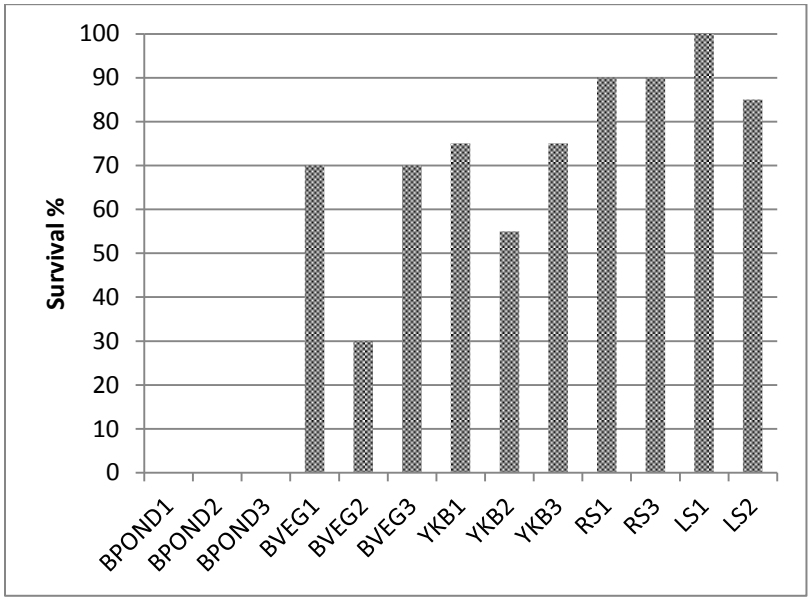
Figure 3-21: The As tissue concentration in the chironomid tissue after the toxicity test. The top shows As tissue concentration from each replicate and the bottom displays the averages and standard deviation. Means with the same letter are not statistically different. BPOND, BVEG, and YKB correspond to the three sample sites while RS and LS are the reference water standard and lab water standard, respectively.

A one-way ANOVA was conducted to determine if the tissue concentration of As varies between sediment exposure from each site. The data were normally distributed for each group, as assessed by Shapiro-Wilk test ($p > .05$); and there was homogeneity of variances, as assessed by Levene's test of homogeneity of variances ($p = 0.430$) after $\log_{10}$ transformation of the data. Data are presented as mean ± standard deviation. Arsenic tissue concentration was significantly different between different sediment exposures ($F(3,12)=74.57$, $p <.0005$). Tissue concentration of As increased from LS (3.45±0.89), to RS (4.78±3.17), to YKBay (15.58 ±3.73), to BVEG (512.41±403.61) (untransformed data). Tukey post-hoc analysis on the transformed data revealed that the increase from LS to YKBay, 0.65 (95%CI, 0.186 to 1.12) was statistically significant ($p=0.006$) as was the increase from LS to BVEG, 2.0 (95%CI, 1.62 to 2.56) ($p<0.0005$). The increase from RS to YKBay, 0.56 ,(95%CI,0.95 to 1.0) was statistically significant ($p=0.017$) as was the increase from RS to BVEG, 2.0 (95%CI, 1.52 to 2.4669) ($p<0.0005$). The increase from YKBay to BVEG was also statistically significant, 1.4 (95%CI,0.96 to 1.9) ($p<0.0005$).

3.5.5.2 Fathead Minnows

The fathead minnows displayed the same trend as the *Chironomid dilutus* where the toxicity is BPOND>BOVEG>YKBAY. Several challenges arose during the maintenance of the fish toxicity test and the quality of the control tests was compromised. One replicate from the RS (RS2) and LS (LS3) control tests had 100% mortality despite not being exposed to As. The unexpected deaths could have been caused by multiple factors stemming from the observation that the air bubblers attached to these toxicity tests were faulty and required constant attention. Failure in the tubes corresponded to the replicates with unexpected 100% mortality. Ammonia build-up and fungal infection may have been responsible for the deaths. Because no statistical difference is seen between the toxicity of the LS and RS standards from the chironomid tests the RS and LS standards can be combined to form a single control group with four replicates. This allows for statistical comparison to a control group to be carried out in spite of the lost replicates.

3.5.5.2.1 Survival



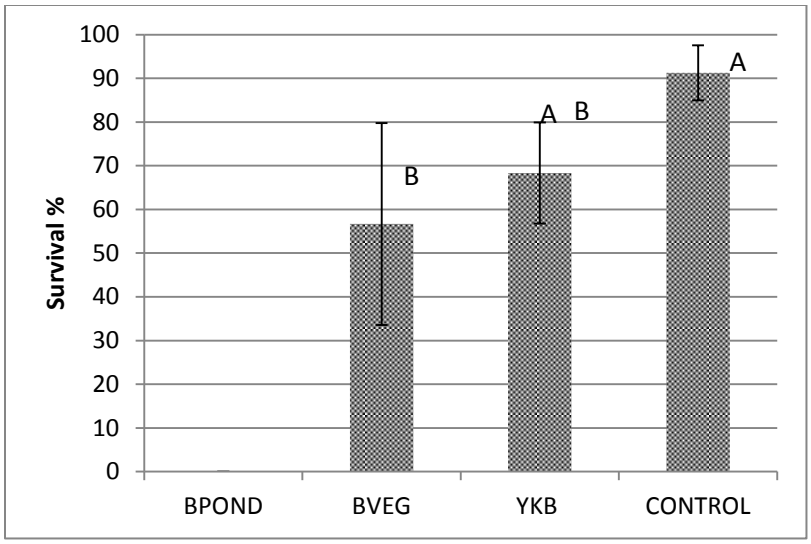


Figure 3-22: Graphs of the survival rate of the fish toxicity tests. The top shows survival % from each replicate and the bottom displays the averages and standard deviation. Means with the same letter are not statistically different. BPOND, BVEG, and YKB correspond to the three sample sites while RS and LS are the reference water standard and lab water standard, respectively.

The assumption of homogeneity of variances was violated, as assessed by Levene's Test of Homogeneity of Variance (p = .034). Data was transformed using the arcsine function which resulted in data with homogeneity of variances (p = 0.557). Survival (%) increased from BPOND (0.0±0.0) to BVEG (56.7%±23.1%) to YKBAY (68.3%±11.5%) to the Control (91.3%±6.3%). Survival % was statistically significantly different between the exposure groups (F(2,7) = 6.216), p = .028). Tukey post-hoc analysis revealed that the increase from BVEG to Control was significant 35% (95% CI (0.6481 to 1.111) (p=.031)).

3.5.5.2.2 Tissue Weight

A one-way ANOVA was conducted to determine if dry tissue mass of the fish varied between exposure groups. Raw data violated the assumption of homogeneity of variances, as assessed by Levene's Test of Homogeneity of Variance (p = .024). Data were then transformed using the $\log_{10}$ function which resulted in data with homogeneity of variances (p=0.153) and was normally distributed for each group when as assessed by Shapiro-Wilk test (p > .05). Individual tissue mass increased from BPOND (0.0±0.0) to Control (0.0014±0.0003) to YKB (0.0017±0.0003) to BVEG (0.002±0.002). Individual tissue mass not significantly different between the exposures (F(2,7) = 1.333), p = .323)

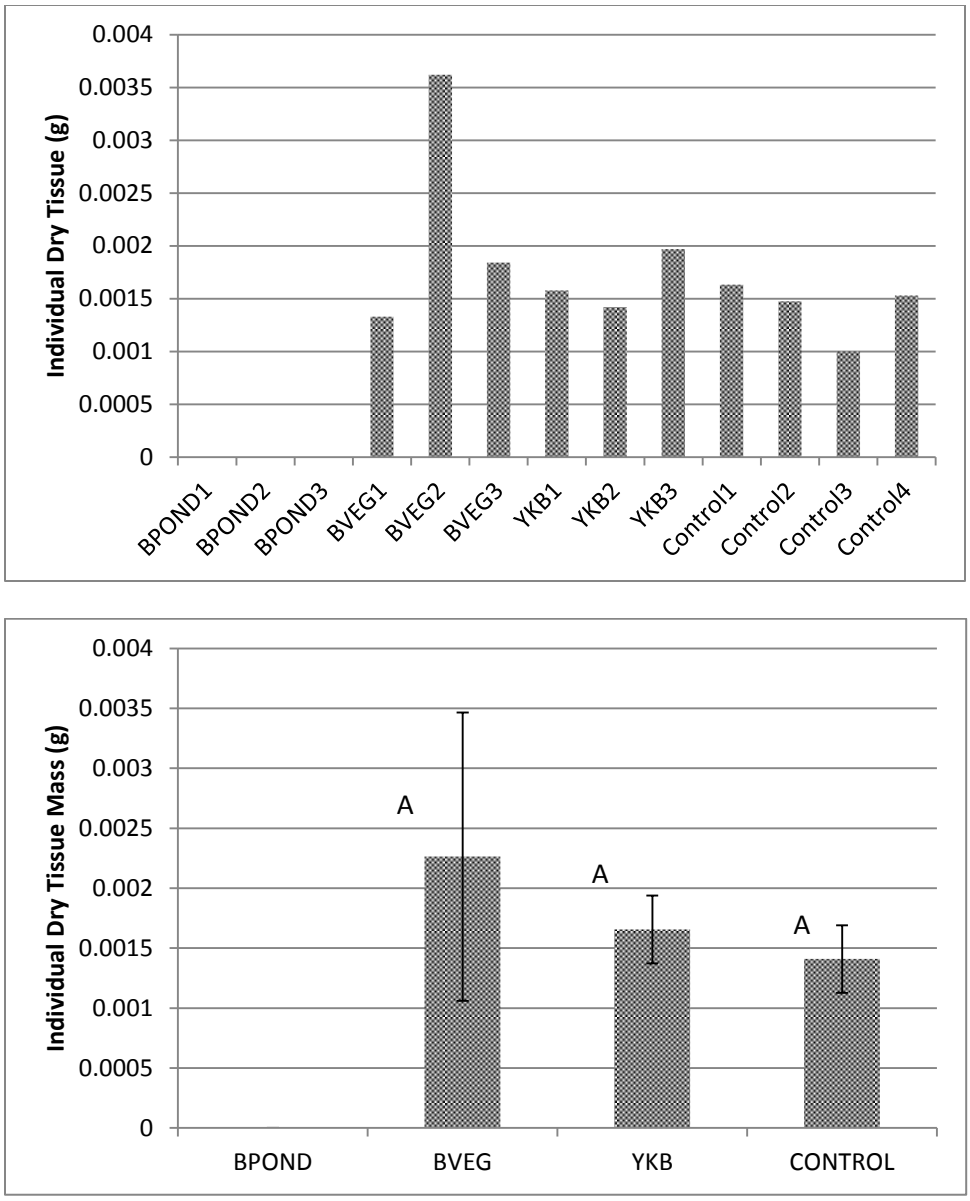


Figure 3-23: The individual dry tissue mass of the fish after the toxicity test. The top shows individual dry tissue mass from each replicate and the bottom displays the averages and standard deviation. Means with the same letter are not statistically different. BPOND, BVEG, and YKB correspond to the three sample sites while RS and LS are the reference water standard and lab water standard, respectively.

3.5.5.2.3 Tissue Arsenic Concentration

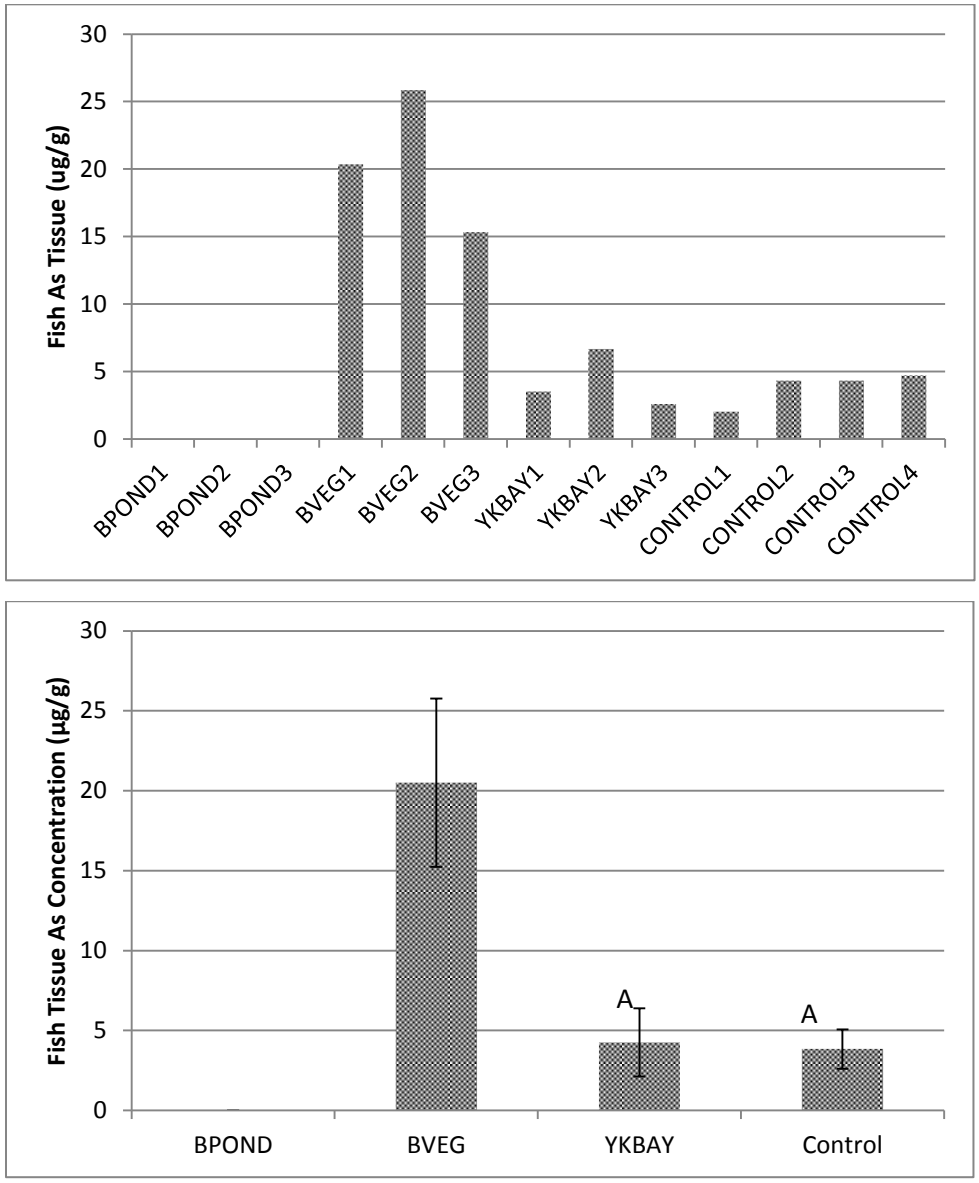


Figure 3-24: The tissue As concentration of the fish after the toxicity test. The top shows Total Dry Tissue Mass from each replicate and the bottom displays the averages and standard deviation. Means with the same letter are not statistically different. BPOND, BVEG, and YKB correspond to the three sample sites while RS and LS are the reference water standard and lab water standard, respectively.

Data were not normally distributed for each group when as assessed by Shapiro-Wilk test ($p < .05$). But did have homogeneity of variance, as assessed by Levene's test of homogeneity of variances ($p=.184$). Failing the requirement for normality a Kruskal-Wallis H test was performed. Arsenic tissue

concentration increased from Control (3847) to YKBay (4258) to BVEG 20501) but the differences were not statistically significant $\chi^2(2) = 5.727$, $p = .057$.

One way ANOVA was then carried out despite the violation of normality. A one-way ANOVA was conducted to determine if the tissue mass of the fish between sediment exposures from each site varied. Data is presented as mean ± standard deviation. Survival rate was significantly different between different sediment exposures, $F(2,7)=28.973$, $p <.0005$. Arsenic Tissue concentration increased from the Control (3847±1230), to YKBay (4258±2128), to BVEG (20502±5259). Tukey post-hoc analysis revealed that the increase from Control to YKBay, 411 (95%CI, -6648 to 7469) was not statistically significant (p=.984). The increase from Control to BVEG, 16655 (95%CI,9597 to 23713) was significant($p<0.001$) as was the increase from YKBay to BVEG, 16243 (95%CI, 8699 to 23789) (p=0.001).

3.5.6 Lysimeter Vs. Minipeeper

The pore-water chemistry results reported in Table 3-2 were measured by lysimeters installed at 10-15cm depths in relatively undisturbed sediments in the field prior to sediment collection. Sediments experienced considerable mixing and opportunity for oxidation during transport and setup of the toxicity tests. Sediment beakers were given 10 days to re-establish equilibrium conditions after transport and prior to toxicity testing. Pore-water can diffuse to the surface during this period, Figure 3-26 shows test sediment pore-water Ni concentration decreased one third its initial concentration over a 200 hour period.

Lysimeters were deployed to investigate whether field conditions were representative of the toxicity test conditions. Mini-peepers were deployed during the toxicity tests to determine the actual pore-water concentrations exposed to the chironomids.

Figure 3-25 shows that lysimeter and mini-peeper measurements differed considerably for As concentration at all three sites. Table 3-13 shows that most of the measurements were found to have higher concentration when measured by lysimeters in the field. Copper had higher concentration when

measured by mini-peeper however the lysimeter concentration was below the detection limit of 0.2. These trends can be influenced by multiple factors. Arsenic concentration is known to vary with sediment depth at all three sample sites (Andrade, 2006; Fawcett, 2009) and triplicate subsampling revealed significant variation (Table 3-4).

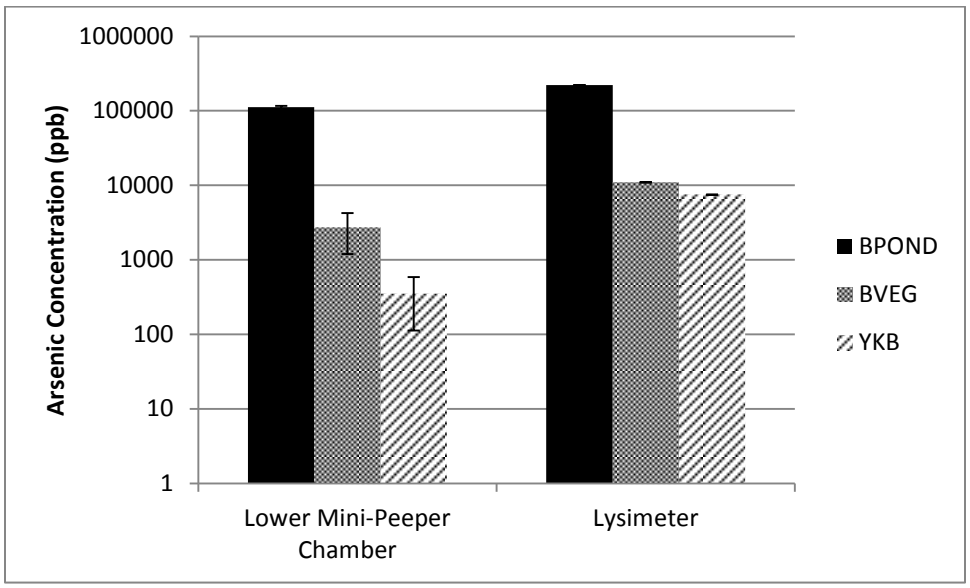


Figure 3-25: The pore- water As concentration at the three sample sites as measured by lysimeters in the field and mini-peepers during the toxicity tests.

	As	Co	Cr	Cu	Ni	Pb	Sb
BPOND	9.9	Ly<DL	6.0	Ly<DL	4.9	Ly+Mp<DL	4.4
BVEG	20.12	62.8	4.4	Ly<DL	20.2	Ly+Mp<DL	2.8
YKB	106.8	19.0	3.4	Ly<DL	3.1	Ly+Mp<DL	4.9

Table 3-13: The difference between peeper and lysimeter measurements expressed as ratios where Ratio=[lysimeter/[mini-peeper]. "Ly<DL" means that the lysimeter measurement was below the detection limit and "Ly+Mp<DL" means both measurements were below the detection limit.

Pore-water concentration in laboratory sediment toxicity tests diffuses into surface water for up to 200 hours after the addition of purified laboratory water while equilibration between pore-water and mini-peeper concentration occurs much faster (<50 hours) (Doig & Liber, 2000). Figure 3-26 shows Ni pore-water concentration decreasing over time in a sediment beaker, even after mini-peeper chambers have equilibrated. Diffusion rates into peeper cells and surface waters is influenced by element speciation and concentration, sediment porosity, and solid-phase adsorbants.

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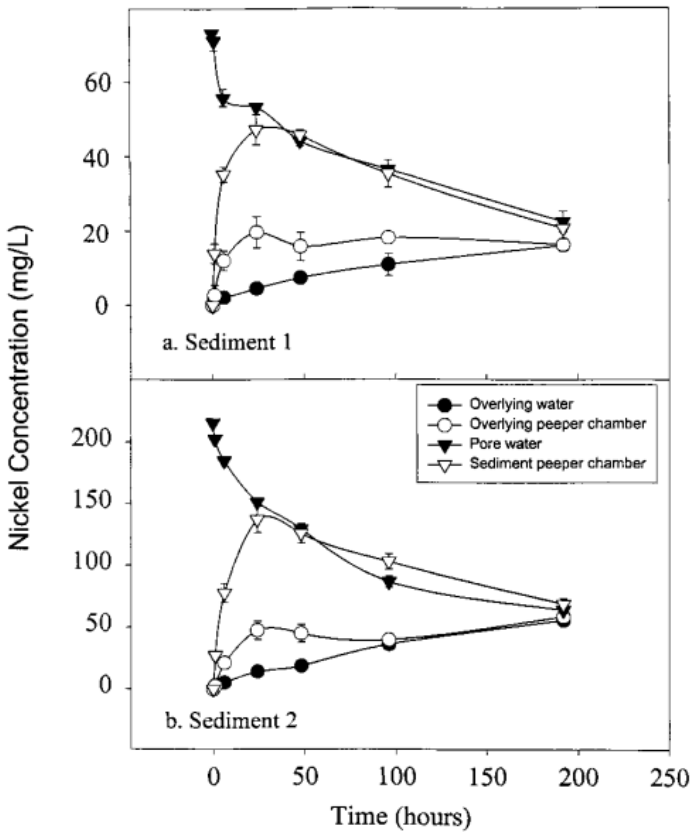


Figure 3-26: Peeper concentration and sediment pore-water concentration from (Doig & Liber, 2000) with two sediments of varying nickel sorption capacity.

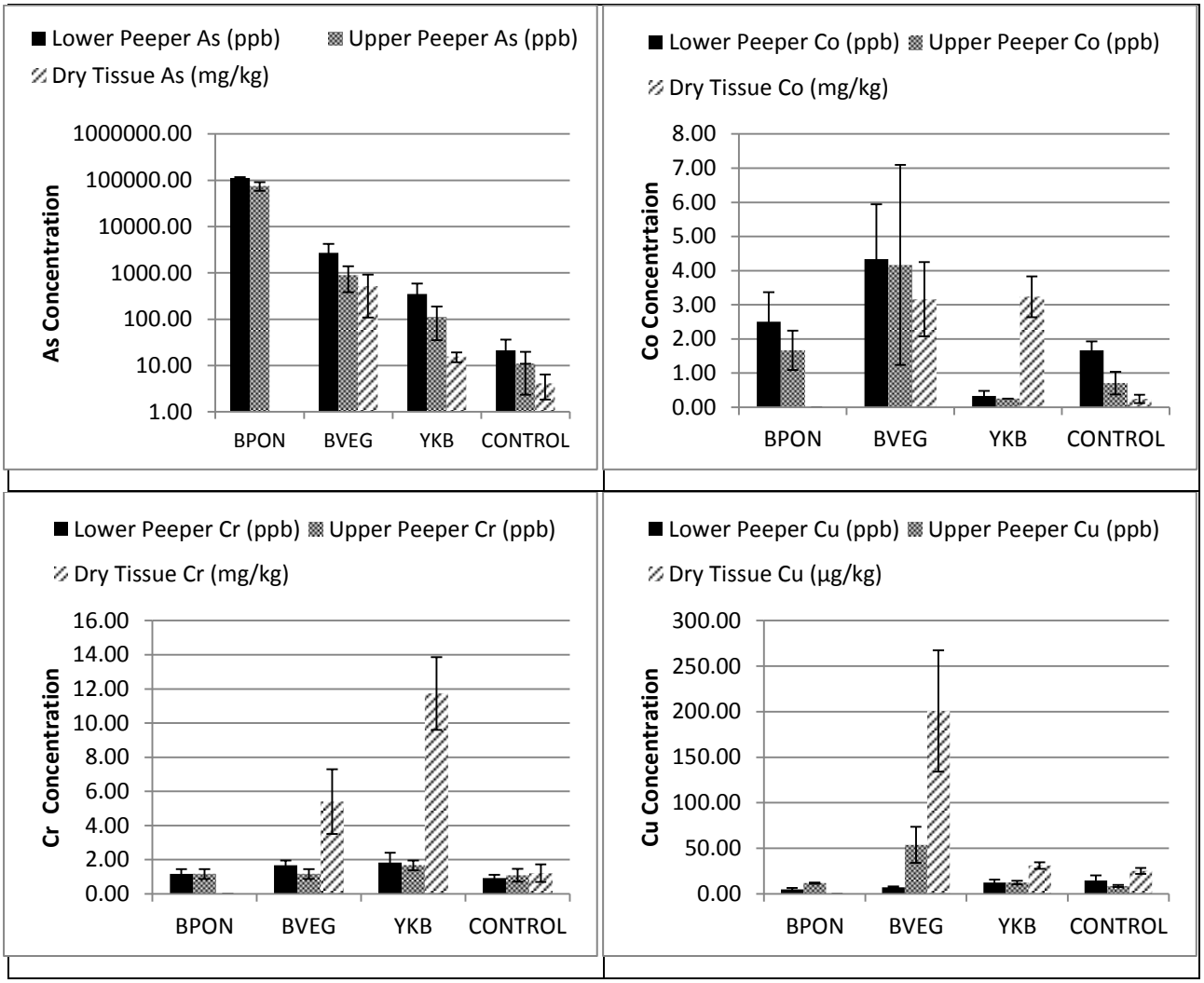
Thus, two factors are contributing to the discrepancy between measurements summarized in Table 3-13. First, pore-water concentration diffuses to the surface during the 10-day equilibration period, lowering mini-peeper measurements. Second, the lysimeter (10-15cm) sampled from much deeper than the mini-peeper (2cm) which may have enriched pore-water (Figure 3-1) that was not collected with the sediments or are not subject to the same rate of flux to the surface.

3.5.7 Bioaccessibility and Bioavailability Measurements Comparison

3.5.7.1 Mini-peeper vs. Tissue

Bioaccessible measurements report the concentration of an element *potentially available* to an organism. Pore-water concentration, DGT measurements, surface water, and soluble solid phase elements are all measurements of bioaccessibility. Bioavailability reports the *actual uptake* of an element into an exposed organism. Tissue concentration measurements are bioavailability measurements.

Pore-water concentration, DGT measurements, surface water, and soluble solid phase elements are most useful when they can be statistically correlated to actual uptake of exposed organisms. Mini-peeper pore-water concentrations are presented alongside chironomid tissue concentration in Figure 3-27. Arsenic in the Great Slave Lake control water was detectable at 9ppb and is bioaccumulated in the control group.



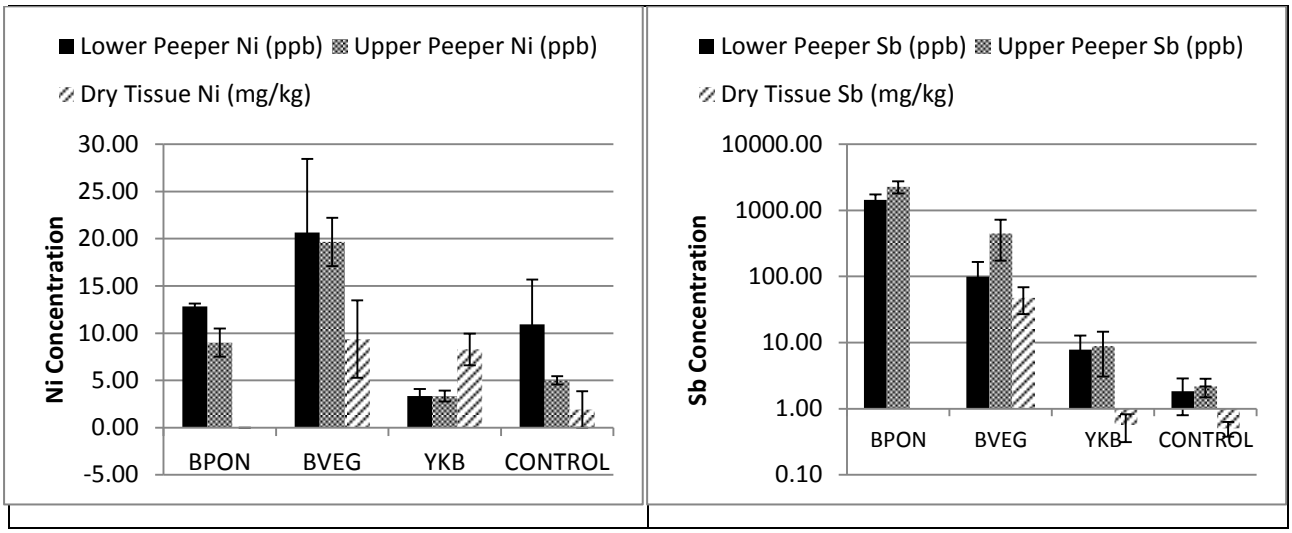


Figure 3-27: Mini-peeper concentration plotted alongside chironomid tissue concentration. n=3 for mini-peeper measurements and n=4 for chironomid tissue concentration.

These graphs illustrate the general trend that upper peeper measurements have reduced concentration and lower peeper elements are more concentrated. Dry tissue concentration could be expected to follow the general trend of agreeing with peeper As concentration, however several anomalies stand out. Co, Cu and Ni all have lower tissue concentration in BVEG tests than YKB tests, despite BVEG having a higher total dissolved element concentration in these peeper-measurements. The cause for this is presently unknown.

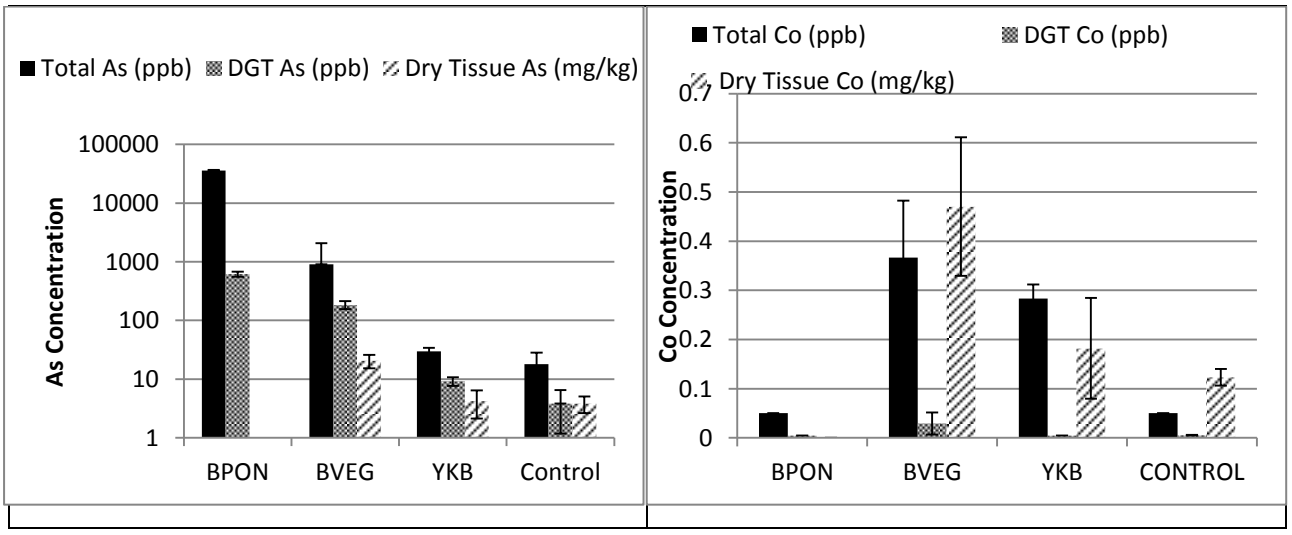
There are several problems with mini-peeper water chemistry data that influence statistical analysis of the results. There is a large variation observed in all of the Baker Outlet Vegetated concentrations. For example, As lower-peeper BVEG values range from 312 ppb to 890 ppb. This is likely caused by the heterogenous nature of the site which is a mixture of sediment and vegetation. During deployment all mini-peepers were inserted so that the bottom dialysis chamber was fully covered by sediment. In the event that the bottom chamber were not fully covered the chamber would fail to measure the pore water concentrations as intended, instead measuring a mix of pore and surface water. The Baker Outlet Vegetated sediments were observed to be very spongy and compressible due to the abundance of organic matter. This spongy texture is believed to have created channels connecting the lower peeper chamber to the surface, diluting some of the chambers to varying degrees.

Statistical analysis of these results did not result in any statistically significant correlation between peeper concentration and tissue concentration.

3.5.8 DGTs and Tissue Concentrations

DGTs offer a more nuanced measurement of bioaccessible element concentration than total dissolved As concentration. DGTs account for binding by strong ligands that can decrease uptake by exposed fish.

As, Co, Cr, Cu, Mn, Ni, Pb, Sb, and Zn measurements were all compared for bioavailability plots as seen in the following graphs. However, elements are not included below when there was no variation in metal concentration across all samples. For example, Zn is not shown because its lower peeper concentration did not vary significantly from 1ppb in any sample.



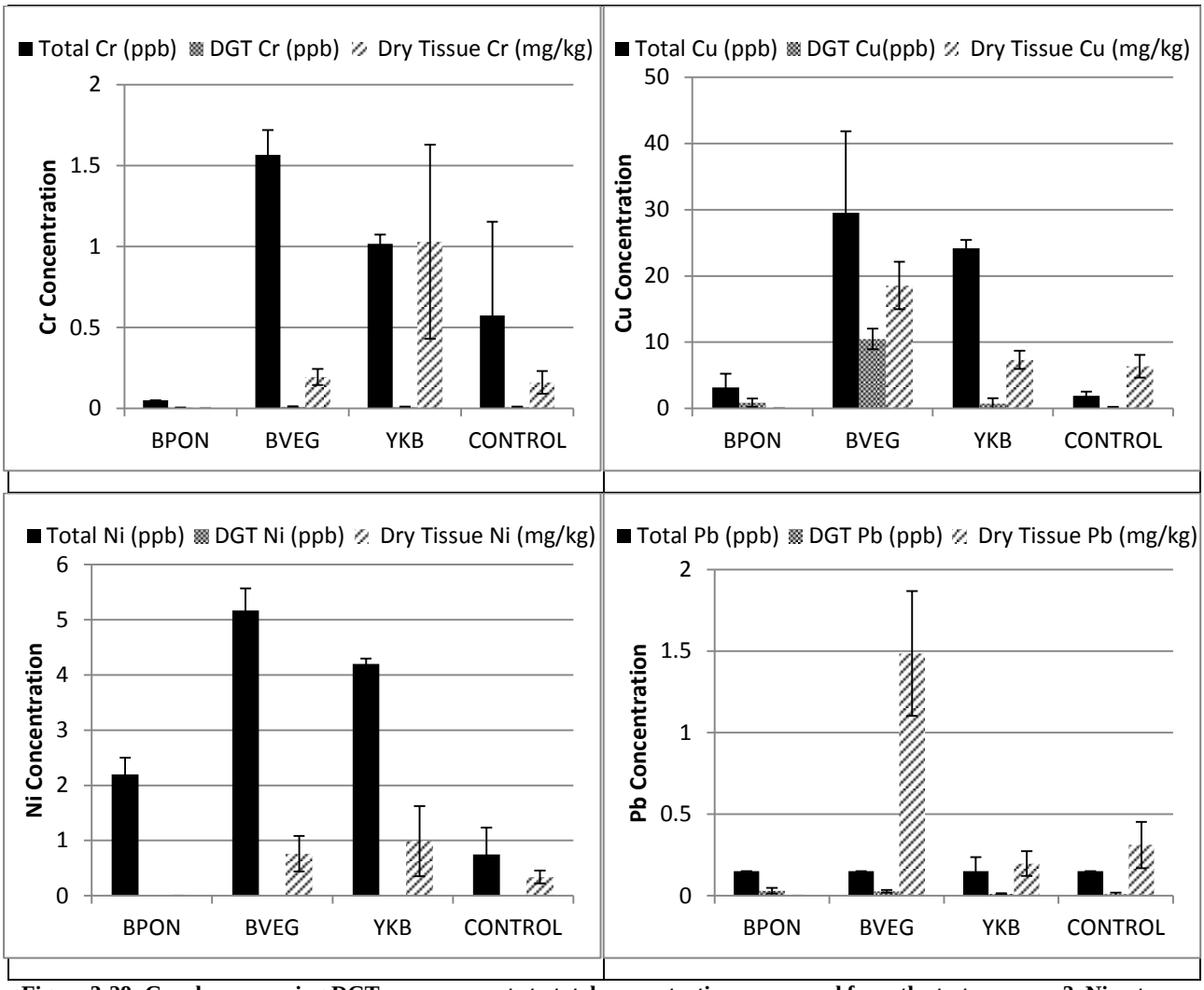


Figure 3-28: Graphs comparing DGT measurements to total concentrations measured from the test cones. n=3. Ni not measured.

Figure 3-28 illustrates the trend between total element concentration, DGT concentration, and dry tissue concentration. Cu shows a reverse trend where DGT Cu is much higher than the total Cu. Contamination from an outside Cu source is expected. There is no similar contamination found within the other elements or samples.

Linear regression and ANOVA was performed in order to judge the quality of the statistical correlation.

Element	F	p	r^2
As	F(1,8)=40.773	<0.0005*	0.836
Co	F(1,8)=4.571	0.065	0.364
Cr	F(1,8)=0.070	0.799	0.009
Cu	F(1,8)=30.565	0.001*	0.793
Mn	F(1,8)=1.932	0.202	0.195
Pb	F(1,8)=9.908	0.014*	0.553
Zn	F(1,8)=0.121	0.737	0.015

Table 3-14: Independent variable DGT concentration and dependent tissue concentration. * indicates statistical relevancy.

Element	F	p	r^2
As	F(1,8)=54.764	<0.0005*	0.873
Co	F(1,8)=69.933	<0.0005*^{x}	0.885
Cr	F(1,8)=0.650	0.443	0.075
Cu	F(1,8)=93.168	<0.0005*	0.921
Pb	F(1,8)=5.453	0.048*^{x}	0.405
Sb	F(1,8)=75.722	<0.0005*	0.915

Table 3-15: Independent variable Total concentration and dependent tissue concentration. * indicates statistical relevancy. ^{x} indicates that the statistical relevancy is a false positive due to measurements below detection limits and low variability of the element in tissue concentrations.

DGTs were deployed for 10 days in the fathead minnow tests. The results can be compared to direct total concentrations that were taken during the test. Only As and Cu showed significant differences in concentration between sediment samples. Additionally, detection limits for the measured DGT eluent were too low for effective measurement. Detection limits negatively affected Cr, Co, and Pb analysis. For example, the detection limit for the Co eluent was 0.1 ppb. All but one measurement for Co were below 0.5 ppb. Thus, DGT measurements for Co had a very low resolution, with all measurements being a multiple of 0.1 ppb.

Dissolved organic carbon (DOC) was measured in the fathead minnow toxicity tests. DOC measurements include humic acid in addition to other carbon compounds. Humic acid concentrations were not directly measured. DOC was highest in BVEG test waters (16.8mg/L) and lowest in the control waters (11.0mg/L). The small range of DOC concentrations (5.8mg/L) suggests that the DOC's impact on As speciation may have been similar in each treatment. Full results are available in Appendix G.

3.5.9 Peepers and Sequential Extractions

Mini-peepers can be used in beakers containing sediment and test organisms. This allows for a direct correlation between pore-water element concentrations and element bioaccumulation in test organisms. It removes the need to set up additional beakers for pore-water extraction and allows for more powerful statistical comparison of tissue concentration and pore-water concentration.

Selective sequential extraction (SSE) data can also be used to assess contaminant lability in the solid phase. As discussed earlier, the BCR method used for these experiments used a three step extraction to isolate (1) exchangeable/acid-extractable metals (2) reducible phases and (3) oxidizable phases.

Of the three extraction steps the first step (using 0.11M acetic acid) extracts the most relevant As. The exchangeable As will be the first to dissolve in the laboratory setting and be exposed to the test organisms. It follows that the first SSE phase may be predictive of pore-water and surface chemistry. Linear regression analysis was performed in order to test this hypothesis.

Element	F	p	r^2
As	F(1,1)=783.01	0.023*	.999
Co	F(1,1)=3.235	0.323	.764
Cr	F(1,1)=8.88	0.206	.899
Cu	F(1,1)=0.045	0.866	.043
Ni	F(1,1)=4.812	0.272	.828
Pb	F(1,1)=24.575	0.127	.961
Sb	F(1,1)=2.75	0.345	.733

Table 3-16: Independent variable is SSE exchangeable element concentration (ppm)and dependent variable is lower peeper concentration (ppb). * indicates statistical relevancy.

Only sequential extractions of As were predictive of pore-water concentrations (r^2=0.999 and $p<0.023$). This analysis is weakened by a small data set restricted by the sediment sampling protocol. Only three points were included in each data analysis. Both mini-peepers and sequential extractions were conducted in triplicate for three sites but the sequential extractions were not conducted on the same sediments that the mini-peepers were deployed in. Instead the sediments were taken in triplicate from the bulk sediments prior to setup of the toxicity tests. This meant that for each sample site the average sequential extraction values had to be compared to the average pore-water concentrations, allowing for

only three data points. If sediments had been sampled directly from the test chambers nine data points would be available for analysis. Before conclusions are drawn regarding the usefulness of the BCR sequential extractions for pore-water prediction the test should be repeated with a larger data set.

3.6 Discussion

3.6.1 Sediment arsenic hosts

Sediment As hosting controls the solubility, bioaccesibility, and Eh and pH stability of the minerals and is thus a major control of the in the toxicity and bioaccumulation study discussed in Section 3.3. Arsenic was found in As_2O_3, roaster-generated Fe-oxides, arsenopyrite, and amorphous Fe root plaque.

3.6.2 Vegetation Roots Arsenic Hosts

There is a clear trend of As and Fe seen in the element map of the horsetail cross sections in Baker Outlet. The sharp edge in the element correlation plot Figure 3-14 indicates a critical ratio that As cannot exceed. µXRD of the As/Fe mixture around the root edge revealed that the elements do not diffract, consistent with the hypothesis that the As/Fe mixture is iron root plaque adsorbing As. Finally, µXANES identified predominantly As(V) and some As(III) which consistent with the stronger binding of As(V) to Fe-oxides at circum-neutral pH.

The Baker Vegetated sediments included organic matter. Prior to testing large sticks, twigs, leaves and roots were manually extracted before any further subsampling or testing was done with them. Only the largest pieces of vegetable matter were removed from the sediments, the majority of the vegetation was left in the sediments.

Bulk XANES revealed that the root plaque found on extracted roots was rich in As(V) and the bulk sediments (containing all but the largest fraction of roots) contained no As(V). The different oxidation states suggests that the root plaques As concentration is small enough to be negligible when measured against the As(III) and As(-I) found in the rest of the sediments.

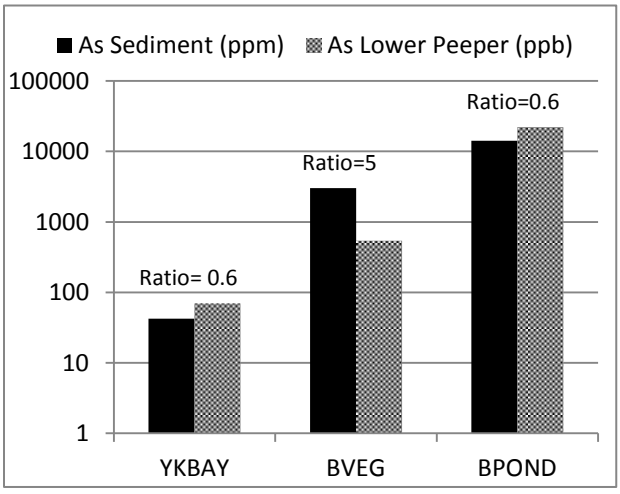
Wetland plant roots, including cattails, are known to sometimes oxidize the root area in the immediate proximity (several hundred microns) of roots and rhizomes, can develop porous tissue that allows enhanced oxygen transport to the roots for respiration (Blute *et al.*, 2004; Ma *et al.*, 2008).

The presence of As(V) in root XANES and absence in BVEG XANES spectrums may suggest that the Cattail roots oxidise As(III) themselves. The alternative to this is that the roots are simply scavenging low levels of As(V) already present in pore-water.

Previous oxidation state mapping of As in Cattail root mapping has shown that there is a slight tendency for As(III) to dominate in the interior of root plaque (which is more highly oxidising than the outer rim) (Blute *et al.*, 2004). At Giant Mine As is not often redox equilibrium with its environment (Figure 3-11) suggesting that the roots are not oxidising As(III).

3.6.2.1 Significance to pore water

The relative concentration of As adsorbed to root plaque is low compared to As in the adjacent sediments. This does not necessarily prevent the root plaque from influencing pore water concentrations. The total amount of As sequestered in root plaque is not significant to total As in the solid phase (3012mg/kg), but it may be significant to the total amount of As dissolved in pore water which is much lower (11 ppm as measured by field lysimeters).



Figures 3-29: As sediment concentration compared to pore-water concentration.

A similar site has been observed where As adsorption to iron oxides has had significant effects. (Blute *et al.*, 2004) examined a strikingly similar system dominated by Cattail roots with pore water concentrations ranging from 0.30 to 0.77 ppm As in sulfidic riverbed sediments. Blute et al. (2004) calculated that release of the adsorbed As would raise the pore water concentration up to 50 times higher than the current levels (44 ppm) in the absence of As redistribution into other solid phases. Blute showed that in a system where 1 gram of root plaque may adsorb a maximum of 200µg As there is a significant reduction in pore water concentration. The following equation was used to calculate the stores of As held in root plaque:

$$Increase\ in\ [As] = Plaque\ [As] \cdot \frac{Plaque\ Volume}{Sediment\ Volume} \cdot Plaque\ Density \cdot \frac{1}{Porosity}$$

To perform this calculation for Baker Outlet would require the ratio of plaque to the bulk sediment as calculated by sequential extractions and microtomography techniques. The riverbed and wetland soils that Blute collected from were composed of sulfidic riverbed sediments composed of silty-sand and iron-reducing wetland peat. The sediments had solid phase As concentrations ranging from 100-10000 mg/kg with pore-water concentration from 5 to 600 ug/L which is strikingly similar to the Giant Mine sediments.

These calculations serve to illustrate the relative size of the As sink in root plaque. Release of the As, should it occur would by gradual and the maximum value calculated above would not be reached. Reductive dissolution of Fe-oxides is a well-known cause of remobilisation for adsorbed As and are the most probable mechanism for remobilisation if disturbed (Nickson *et al.*, 2000).

3.6.3 Arsenic Trioxide Dating and Transformation

Arsenic trioxide was observed in Baker Pond and Baker Outlet sediments, but not in the Yellowknife Bay Sediments. The mineral made up a significant As host in Baker Pond where it represented the majority of manually identified As grains. Baker Outlet had much less As_2O_3present, only 9 As_2O_3 grains were found using an automated search using MLA software.

Arsenic trioxide is the most soluble As host identified in the sampled sediments. It is likely responsible for the elevated concentration in Baker Pond as well as the 100% mortality observed in exposed test organisms.

3.6.4 Toxicity Test Results

The Yellowknife Bay sediments were found to not be statistically different from the control groups. Of the three end points (survival, tissue mass, As tissue concentration) for both test organisms, only one test revealed a statistically significant difference between Yellowknife Bay Foreshore sediments and the control groups for the *Chironomous dilutes* tests. All other endpoints for the YKB endpoints were not significantly different from the control sands.

Baker Pond displayed 100% toxicity to all exposed test organisms. This made the endoipoint data from these sediments unsuitable for statistical analysis which require properties such as homogeneity of variance and be normally distributed. Despite not meeting these requirements statistical requirements the Baker Pond sediments' toxicity is clearly much greater than the others'.

Mortality, As uptake, and tissue mass results are consistent throughout the toxicity tests with one significant exception. Figure 3-23 illustrates a surprising result where individual fish tissue mass increased with As uptake and toxicity. It may be that the surviving fish were able to consume more food under less competitive conditions.

3.6.5 Methods of Arsenic Bioaccessibility Measurement

3.6.6 DGTs

Statistical analysis of DGT As concentrations and As fathead minnow tissue concentrations revealed that that the DGTs are capable of predicting tissue uptake. Through linear regression and the f-test it was found that 83.6% of variation in tissue concentration As was explained by DGT As.

The same was found for Cu and Pb, DGTs were able to predict uptake by the fathead minnows. Co, Cr, Mn, and Ni were at or near detection limits when analysed and could not predict uptake.

3.6.6.1 Water Concentration (Fish Cones)

Statistical analysis of direct measurement of aqueous As concentrations and As fathead minnow tissue concentrations revealed that that the direct measurements are capable of predicting tissue uptake. Through ANOVA and the f-test it was found that 87.3% of variation in tissue concentration As was explained by total As concentration.

The same was found for Co, Cu, Pb and Sb which were able to predict uptake by the fathead minnows. Cu and Sb both had a higher r^2 value than the equivalent DGT test, suggesting better prediction and correlation. Co, is however a false result and is below the detection limit and Pb correlation was lower than in the DGT test (r^2=0.41 compared to 0.53). Chromium was at also at detection limits when analysed.

Small number statistics may be responsible for the total water concentrations being better predictors of uptake than DGTs. Larger sample sets would clear up this uncertainty and make the results more robust. Results are consistent with (Roulier *et al.*, 2008) who also found that uptake was best predicted by bulk chemistry data in chironomids.

3.6.6.2 Mini-peepers

Mini-peeper deployment in Baker Outlet sediments was challenging due to the spongy vegetated characteristics. It is suspected that the porous nature of the vegetation rich sediments prevented a strong "soil seal" from forming above the lower chamber, providing channels for pore water to diffuse to the surface. Diffusion to the surface would create a larger variance in peeper measurements from Baker Outlet and cause heteroscedasticity.

Mini-peepers were found to not be able to statistically predict uptake in chironomids. This is a surprising result since mini-peepers are the most direct measure of sediment pore water that the chironomids were exposed to. Heteroscedasticity means that the variance in the errors is variable across all the

measurements. Transformation techniques including square root and logarithmic transformation did not remove the heteroscedasticity.

Shown in Figure 3-30 is a graphical representation of As peeper and tissue concentration heteroscedasticity. If homoscedasticity was present the distribution of dots would be even around the whole plot. Instead there are three large outliers caused by Baker Outlet samples.

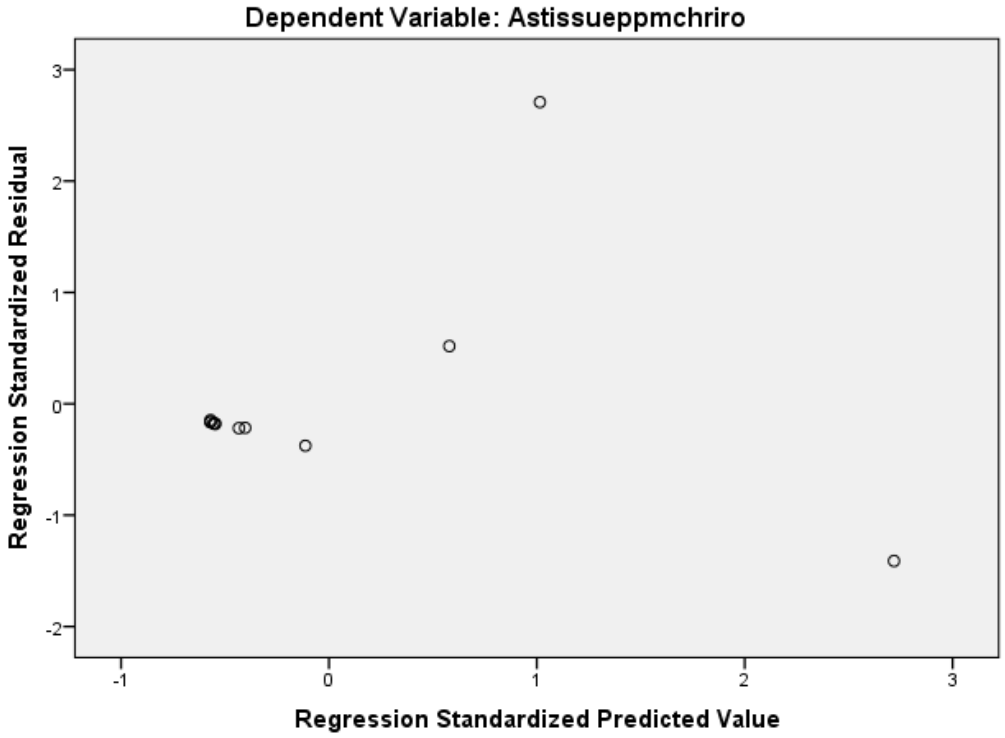


Figure 3-30: A plot graphically showing the heterodascity of the mini-peeper and tissue As concentrations.

Chapter 4

Conclusions and Future Work

4.1 Conclusions

Tailings impacted sediments at Giant Mine are elevated in As and other trace metals. Arsenic concentration in sediments exceeds the interim sediment quality guidelines (5.9 mg/kg) by over 2000 times at the most contaminated site, Baker Pond. ESEM and synchrotron mineralogical analysis identified arsenopyrite, Fe-oxides, Fe-root plaque, and As_2O_3 as As hosts.

The As hosts identified during micro analysis were compared to sequential extractions and bulk XANES data to identify the primary hosts at each sample site. Baker Pond As was predominantly hosted in As_2O_3 and Fe-oxides. While As_2O_3 at Giant is less soluble than pure As_2O_3 due to trace Sb content (SRK 2002) the highly As concentrated pore-water at Baker Pond (221ppm) may be indicative of its slow dissolution. Baker Outlet Vegetated As was predominantly hosted in arsenopyrite, though amorphous Fe oxides may be playing a role in supressing pore-water As concentration. Yellowknife Bay Beach sediments were predominantly hosted at low concentration in Fe-oxides and arsenopyrite and had a corresponding low As concentration in the pore-water.

The Human and Ecological Risk Assessment (SENES 2002) assumed that sedimentary As was hosted as arsenopyrite and assigned a bioavailability of 50% for calculation and prediction purposes. The hosts identified in this research reveal the SENES assumption was an oversimplification of the complex As speciation found in Giant Mine sediments. Assuming all solid phase As is arsenopyrite could lead to the underestimation of toxicity in sites impacted by more bioavailable hosts such as As_2O_3 and overestimation at sites where there is a significant As sink such as at Baker Outlet with the Fe-oxide root plaque. More recent research by Golder (2013) overcame the limitations of this erroneous bioavailability assumption by conducting full sediment exposure toxicity tests which are not influenced by assumptions of contaminant hosting.

In this work 10-day *Chironomus dilutes* and 21-day *Pimephales promelas* toxicity tests revealed that the sampled sediments had a wide range of toxicities. Baker Pond had 100% mortality in both *Chironomus dilutes* and *Pimephales promelas* toxicity tests while Yellowknife Bay Beach sediments were not statistically different from the control groups. An additional test using Baker Pond sediments diluted to 10% concentration also showed 100% mortality for both test organisms. Baker Outlet Vegetated sediments had intermediate toxicity that was statistically different from the other sites.

Mini-peepers and DGTs and were deployed directly into the *Chironomus dilutes* and *Pimephales promelas* toxicity test chambers, respectively. Deployment in the test beakers allowed for direct correlation of each method to contaminant bioaccumulation. As tissue concentrations in *Chironomus dilutes* and *Pimephales promelas* was compared to total aqueous, DGT, mini-peeper and sequential extraction results using linear regression and ANOVA statistics. The statistical analysis was also conducted for Co, Cr, Cu, Ni, Pb, Zn, and Sb. These other metal/metalloids were not always suitable for analysis due to constraints caused by detection limits. Only Cu and Sb concentrations were reliably above detection limits for all measurements.

DGTs were deployed in *Pimephales promelas* test beakers for the last 10 of the 21 day exposure period. DGT measurements of As (r^2=0.836 and p<0.0005), Cu (r^2=0.793 and p=0.001), and Pb (r^2=0.553 and p=0.014) were found to be predictive of their corresponding tissue concentrations in the *Pimephales promelas*. DGT measurements of Co were below the detection limit. Water samples were taken directly from the *Pimephales promelas* test beakers for comparison to DGT measurements at the setup and takedown of the 21 day exposure period. Arsenic concentration increased an average of 21% over the duration of the test. Total concentration measurements of As (r^2=0.873 and p<0.0005), Cu (r^2=0.921 and p<0.0005), and Sb (r^2=0.915 and p<0.0005) were found to be predictive of corresponding tissue concentrations in the *Pimephales promelas*.

DGTs were found to be slightly less predictive or As uptake in *Pimephales promelas* during toxicity tests than were total element concentrations with a difference in r^2 values of 0.037. This result is consistent with Roulier *et al.* (2008) who also found marginally better prediction with total water

concentrations over DGT concentrations. This difference may be too small to be meaningful. Detection limits affected measurements of the trace metals Cr, Co, and Pb. Arsenic measurements were well above detection limits.

Mini-peeper deployment in Baker Outlet sediments in the chironomid toxicity test was challenging due to their spongy and vegetated character. It is suspected that the spongy and heterogeneous nature of the vegetation rich sediments prevented a "soil seal" from forming above the lower chamber, providing channels for pore water to diffuse to the surface. Arsenic measurements were highly variable for Baker Vegetated lower peeper measurements.

Mini-peepers were unable to be statistically linked to tissue concentrations using linear regression and ANOVA analysis. Mini-peeper measurements were not shown to be either statistically correlated, or uncorrelated. Rather, statistical analysis using linear regression was unsuitable for the mini-peeper data. Transformation of the data did not improve its suitability. The mini-peeper data was heteroscedastic meaning the variance in the errors was inconsistent across measurements. While heteroscedastic data cannot be analysed by linear regression and ANOVA, a general trend was observed where lower peeper concentrations increased with sediment and tissue concentrations. The results are likely caused by the highly variable mini-peeper measurements in the Baker Outlet Vegetated sediments.

Despite the lack of correlation between mini-peeper measurement and *Chironomus dilutes* tissue concentration. Mini-peepers are still the most direct measure of conditions within the toxicity test chambers. In this work lysimeter pore-water concentrations were observed to be an uncorrelated to pore-water concentration in the toxicity test chambers, suggesting that field measurements are not suitable for correlation to laboratory toxicity test measurements. Measured by mini-peepers during the toxicity tests, pore-water concentrations of As were found to vary from lysimeter measurements by up 100 times.

4.2 Recommendations for Future Work

- Measure the total amount of As sequestered in horsetail root plaque within the Baker Outlet Vegetated ecosystem. Arsenic concentrations in root plaque can be measured through tomographic and sequential extraction based techniques. Additionally, the significance of the root plaque on As pore-water concentrations should be investigated.
- Use Mineral Liberation Software (MLA) to quantitatively measure the abundance of the As hosts at each field sites and compare to μXANES and sequential extraction-based interpretations. MLA has the power to reduce the ambiguity from these interpretations.
- Investigate the disagreement between lysimeter and mini-peeper measurements further. The current results are ambiguous as to whether pore-water concentrations are not re-established in the lab or that lysimeter-measurements are not sampling pore-waters representative of mini-peeper depths (10-15cm vs. 2cm) High resolution mini-peepers could be should to investigate if depth profiles are established within the test chambers. Mini-peepers should be also deployed in both the field and lab as a control.
- Furthermore, the 10-day equilibration period prior to testing should be examined using mini-peepers tracking pore-water concentration over regular sampling intervals until equilibrium with both the surface and sediment phase is reached.
- Asses methods of sediment preparation in highly vegetated sediments that will allow for proper use of mini-peepers. Asses mini-peeper correlation to tissue concentrations in sediments without confounding vegetation fractions.
- Determine the spatial limits of the highly contaminated Baker Pond sediments. The Baker Creek Remediation Plan identified six other sites with 100% mortality for benthic organisms. The total surface area of these to be assessed in order to best evaluate potential remediation and mitigation options.

- Explore DGT, mini-peeper and total element concentration correlations to tissue concentration in toxicity tests with larger data sets to find if DGT measurements are able to improve on total element correlation to tissue concentration.

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Appendix A: Sediment Results

Bulk chemistry results

Elemental Results

All elements measured by ACME Laboratories bulk chemistry *aqua regia* ICP-MS results. High As in BPOND samples were above detection limits wand were re-tested at the Queen's University Analytical Services Unit using *aqua regia* ICP-AES.

Analyte	Mo	Cu	Pb	Zn	Ag	Ni	Co	Mn	Fe	As	U	Au	Th	Sr	Cd	Sb	Bi	V
Unit	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	mg/kg	mg/kg	µg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
YKBAY-1	0.2	26.31	10.56	63.5	0.106	30.4	13.1	452	2.84	39	2.3	0.0411	15.4	38.9	0.1	0.56	0.26	45
YKBAY-2	0.3	27.36	10.89	65.4	0.206	32.2	13.3	464	3	46.6	2.3	0.4084	15.1	38.5	0.13	0.85	0.26	45
YKBAY-3	0.26	26.65	10.81	67.9	0.093	32.9	13.7	467	2.96	41.9	2.3	0.0177	15	37.1	0.12	0.76	0.24	45
BVEG-1	2.69	923.97	172.94	498.3	4.826	77.1	24.1	271	2.73	2373.9	3.9	5.8073	7.2	37.5	1.76	330.55	0.38	38
BVEG-2	3.43	1107.81	137.95	670	4.688	102	31.3	229	2.47	4346.9	4.4	5.4947	8.1	37.6	2.5	301.9	0.44	33
BVEG-3	2.15	825.99	161.74	481.8	4.822	70.9	21.7	264	2.7	2316	3.5	4.1367	8	34.5	1.64	305.24	0.35	37
BPOND-1	0.45	34.75	52.42	87.7	1.257	29.7	10.9	284	2.18	>10000.0	2.3	1.027	9.3	61	0.42	283.74	0.33	33
BPOND-2	0.47	34.72	47.26	86.7	1.135	28.6	10.7	287	2.11	>10000.0	2.4	0.9311	8.7	59.1	0.37	289.14	0.31	32
BPOND-3	0.51	34.1	51.33	82	1.298	28.5	10.2	272	2.1	>10000.0	2.4	1.0473	8.7	59.1	0.42	278.46	0.32	31

Analyte	Ca	P	La	Cr	Mg	Ba	Ti	B	Al	Na	K	W	Sc	Tl	S	Hg	Se	Te	Ga
Unit	%	%	mg/kg	mg/kg	%	mg/kg	%	mg/kg	%	%	%	mg/kg	mg/kg	mg/kg	%	µg/kg	mg/kg	mg/kg	mg/kg
YKBAY-1	0.51	0.063	39.7	42.9	0.98	219.2	0.107	<20	1.92	0.043	0.44	0.2	5.9	0.29	<0.02	0.048	<0.1	<0.02	7.5
YKBAY-2	0.5	0.064	42	43.5	0.98	229.5	0.107	<20	1.91	0.04	0.44	0.6	5.6	0.27	<0.02	0.035	<0.1	<0.02	7.5
YKBAY-3	0.49	0.065	40.7	43.7	0.97	223.2	0.106	<20	1.89	0.039	0.44	0.4	5.6	0.27	<0.02	0.033	<0.1	0.03	7.6
BVEG-1	0.93	0.043	24	35.6	0.8	80.3	0.037	<20	1.21	0.028	0.12	14.8	4	0.17	0.52	0.176	1.1	0.06	4.2
BVEG-2	0.85	0.045	26.2	33.9	0.71	73.1	0.035	<20	1.09	0.027	0.1	11.6	4.1	0.16	0.67	0.207	1.2	0.04	3.8
BVEG-3	0.81	0.043	24.1	36.6	0.79	92.7	0.041	<20	1.26	0.026	0.14	12.9	4.2	0.18	0.51	0.2	1.2	0.04	4.5
BPOND-1	0.56	0.049	25.4	35	0.6	138.9	0.046	<20	1.39	0.026	0.22	0.2	3.8	0.17	0.04	4.698	0.5	0.1	5.4
BPOND-2	0.56	0.048	24.4	35	0.58	141.8	0.046	<20	1.34	0.026	0.22	0.2	3.7	0.16	0.04	2.599	0.4	0.09	5.1
BPOND-3	0.56	0.049	24.9	34.4	0.57	132.6	0.044	<20	1.36	0.026	0.21	0.2	3.8	0.15	0.04	2.772	0.5	0.1	5

Sample	As
Unit	mg/kg
BPOND-1	12500
BPOND-2	12700
BPOND-3	17200

Appendix B: Pore-Water Results

Major Cation, Anion and Trace Metals

Trace metal/metalloid in pore-water
Sampled by suction lysimeter, measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS by the Analytical Services Group at CanmetMINING. All values in mg/L.

	As	Co	Cr	Cu	Ni	Pb	Sb	Zn
YKBAY-1	7.48	0.0019	0.0012	< 0.0022	0.0020	< 0.0002	0.0078	< 0.024
YKBAY-2	7.51	0.0019	0.0012	< 0.0022	0.0021	< 0.0002	0.0076	< 0.024
YKBAY-3	7.5	0.0019	0.0013	< 0.0022	0.0021	< 0.0002	0.0075	< 0.024
BOVEG-1	11.12	0.0541	0.0015	< 0.0022	0.0830	< 0.0002	0.0557	< 0.024
BOVEG-2	10.91	0.0545	0.0014	< 0.0022	0.0831	< 0.0002	0.055	< 0.024
BOVEG-3	10.88	0.0546	0.0015	< 0.0022	0.0839	< 0.0002	0.0548	< 0.024
BPOND-1	220.2	0.0038	0.0014	< 0.0022	0.0125	< 0.0002	1.266	< 0.024
BPOND-2	222.4	0.0038	0.0014	< 0.0022	0.0127	< 0.0002	1.275	< 0.024
BPOND-3	220.3	0.0038	0.0014	< 0.0022	0.0124	< 0.0002	1.272	< 0.024

Major cations in pore-water
Sampled by suction lysimeter, measured by method 3VIXXX1 using an a Varian Viasta ICP-AES by the Analytical Services Group at CanmetMINING. All values in mg/L.

	Ca	Fe	K	Mg	Mn	Na
YKBAY	93.54	0.127	6.58	38.99	0.989	26.57
BOVEG	155.4	20.53	5.6	37.28	0.815	36.4
BPOND	137.3	0.651	9.43	41.64	0.43	32.01

Major anions in pore-water
Sampled by suction lysimeter, measured by method 2ICIC3 using an IonPac Analytical Column AS14 on a Dionex – ICS 160. All values in mg/L.

	Cl	NO_3	PO_4	SO_4
YKBAY	22	< 0.06	< 0.29	81
BOVEG	80	13	< 0.29	270
BPOND	114	< 0.06	< 0.29	263

Arsenic speciation in pore-water
Sampled by suction lysimeter, measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS by the Analytical Services Group at CanmetMINING. All values in µg/L.

	Preservation by Chilling			Preservation by Chilling and HCL			Preservation by Freezing		
	YKBAY	BOVEG	BPOND	YKBAY	BOVEG	BPOND	YKBAY	BOVEG	BPOND
As(III)	6593.0	5000.0	198100.0	6624.0	8637.0	185400.0	6624.0	8637.0	185400.0
As(V)	356.2	851.7	10430.0	129.8	1767.0	10180.0	129.8	1767.0	10180.0
As (T)	7496.7	10970.0	220966.7	7496.7	10970.0	220966.7	7496.7	10970.0	220966.7

Appendix C: Surface Water Results

Major Cation, Anion and Trace Metals

Trace metal/metalloid in surface water
Measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS by the Analytical Services Group at CanmetMINING. All values in mg/L.

	As	Co	Cr	Cu	Ni	Pb	Sb	Zn
GSLSW-1	0.00387	< 0.0002	0.0013	< 0.0022	< 0.0006	< 0.0002	0.0005	< 0.024
GSLSW-2	0.00325	< 0.0002	0.0012	< 0.0022	< 0.0006	< 0.0002	0.0004	< 0.024
GSLSW-3	0.0027	< 0.0002	0.0012	< 0.0022	< 0.0006	< 0.0002	0.0004	< 0.024
YKBAY-1	0.1	< 0.0002	0.0012	< 0.0022	< 0.0006	< 0.0002	0.0019	< 0.024
YKBAY-2	0.1	< 0.0002	0.0012	0.0030	< 0.0006	< 0.0002	0.0016	< 0.024
YKBAY-3	0.0951	< 0.0002	< 0.0002	< 0.0022	< 0.0006	< 0.0002	< 0.0003	< 0.024
BOVEG-1	0.134	0.003	0.0013	< 0.0022	0.0078	< 0.0002	0.1491	< 0.024
BOVEG-2	0.136	0.0031	0.0012	< 0.0022	0.0078	< 0.0002	0.1502	< 0.024
BOVEG-3	0.134	0.0031	0.0013	< 0.0022	0.0080	< 0.0002	0.1499	< 0.024
BPOND-1	0.279	0.0025	0.0013	< 0.0022	0.0086	< 0.0002	0.1344	< 0.024
BPOND-2	0.283	0.0024	0.0013	< 0.0022	0.0088	< 0.0002	0.1347	< 0.024
BPOND-3	0.283	0.0024	0.0013	< 0.0022	0.0088	< 0.0002	0.133	< 0.024

Major cations in surface water
Measured by method 3VIXXX1 using an a Varian Viasta ICP-AES by the Analytical Services Group at CanmetMINING. All values in mg/L.

	Ca	Fe	K	Mg	Mn	Na
GSLSW	7.9	0.0063	1.14	2.53	<0.0006	2.74
YKBAY	9.25	0.0115	1.23	3.02	0.0123	2.66
BOVEG	173.7	0.0537	4.95	40.34	0.0295	68.36
BPOND	140.4	0.0429	4.16	32.72	0.0151	53.89

Major anions in surface water
Measured by method 2ICIC3 using an IonPac Analytical Column AS14 on a Dionex – ICS 160. All values in mg/L.

	Cl	NO3	PO4	SO4
GSLSW	4	< 0.06	< 0.29	5.4
YKBAY	3.7	< 0.06	< 0.29	5.1
BOVEG	176	2.21	< 0.29	444
BPOND	142	1.9	< 0.29	349

Arsenic speciation in pore-water
Measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS by the Analytical Services Group at CanmetMINING. All values in µg/L.

	Preservation by Chilling			Preservation by Chilling and HCL			Preservation by Freezing		
	YKBAY	BOVEG	BPOND	YKBAY	BOVEG	BPOND	YKBAY	BOVEG	BPOND
As(III)	< 6.7	< 6.7	< 6.7	7.7	> 7.9	9.5	N/A	6.7	N/A
As(V)	80.9	93.9	234.6	75.9	96.0	234.6	N/A	105.6	N/A

Appendix D: Toxicity Test Endpoint Data

Survival, Tissue Mass, Tissue Concentration

Chironomus dilutes survival, tissue mass and arsenic tissue concentration

	Survival (of 10)	Tissue Mass (mg)	Tissue [As] (mg/kg)
BPOND1	0	N/A	N/A
BPOND2	0	N/A	N/A
BPOND3	0	N/A	N/A
BPOND4	0	N/A	N/A
BVEG1	5	2.78	389.78
BVEG2	5	4.83	1098.91
BVEG3	3	1.76	175.40
BVEG4	2	1.66	385.53
YKB1	6	11.17	16.50
YKB2	8	9.86	16.08
YKB3	6	8.82	10.42
YKB4	4	4.4	19.33
RS1	6	10.95	2.68
RS2	7	10.13	9.38
RS3	10	11.92	4.40
RS4	10	10.26	2.66
LS1	10	10.27	2.56
LS2	8	9.98	4.37
LS3	6	8.2	4.06
LS4	6	9.31	2.82

Pimephales promelas tissue mass and arsenic tissue concentration

	Survival (of 20)	Tissue Mass (mg)	Tissue [As] (mg/kg)
BPOND1	0	N/A	N/A
BPOND2	0	N/A	N/A
BPOND3	0	N/A	N/A
BVEG1	14	18.6	20.34234
BVEG2	6	21.72	25.83909
BVEG3	14	25.78	15.32438
YKB1	15	23.65	3.522939
YKB2	11	15.64	6.65649
YKB3	15	29.54	2.594787
RS1	18	29.41	2.020741
RS2	0	N/A	N/A
RS3	18	26.53	4.329815
LS1	20	19.97	4.32987
LS2	17	25.98	4.70843
LS3	0	N/A	N/A

Appendix E: Mini-peeper Measurements

Trace Metals, Arsenic Speciation

Arsenic speciation in upper chamber mini-peeper measurements
Measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS by the Analytical Services Group at CanmetMINING. All values in µg/L.

ppb	As (III)	As (V)
BPON1U	27.3	92850.00
BPON2U	75.10	71860.00
BPON3U	41.90	63370.00
BVEG1U	9.10	495.60
BVEG2U	11.50	777.70
BVEG3U	10.0	246.90
YKB1U	< 5.2	46.20
YKB2U	< 5.2	39.70
YKB3U	< 5.2	34.50
RS1U	< 5.2	12.30
RS2U	< 5.2	17.20
RS3U	< 5.2	20.80
LS1U	< 5.2	< 6.6
LS2U	< 5.2	< 6.6
LS3U	< 5.2	< 6.6

Arsenic speciation in lower chamber mini-peeper measurements
Measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS by the Analytical Services Group at CanmetMINING. All values in µg/L.

ppb	As+3	As+5
BPON1L	88270	31460
BPON2L	41570	76270
BPON3L	65360	46080
BVEG1L	417.9	2391
BVEG2L	1885	2292
BVEG3L	5354	4072
YKB1L	< 5.2	33.40
YKB2L	< 5.2	33.90
YKB3L	< 5.2	45.40
RS1L	5.4	12.40
RS2L	6.8	13.30
RS3L	< 5.2	14.00
LS1L	< 5.2	< 6.6
LS2L	< 5.2	< 6.6
LS3L	< 5.2	< 6.6

Trace metal/metalloid in upper peeper chambers

Measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS by the Analytical Services Group at CanmetMINING. All values in µg/L.

	As	Co	Cr	Cu	Ni	Pb	Sb	Zn
BPON1U	93000.00	2.00	1.50	11.50	10.50	< 0.5	1993.00	< 3.5
BPON2U	69200.00	2.00	1.00	11.50	9.00	1.00	2017.00	< 3.5
BPON3U	63600.00	1.00	1.00	12.50	7.50	< 0.5	2833.50	< 3.5
BVEG1U	471.50	3.00	1.50	72.50	19.00	3.00	763.00	48.00
BVEG2U	744.50	2.00	1.00	55.50	17.50	< 0.5	293.00	9.00
BVEG3U	1448.00	7.50	1.00	33.00	22.50	< 0.5	286.50	27.50
YKB1U	199.00	< 0.5	1.50	12.00	3.00	< 0.5	15.50	< 3.5
YKB2U	58.00	< 0.5	1.50	10.50	3.00	< 0.5	5.50	< 3.5
YKB3U	77.50	< 0.5	2.00	14.50	4.00	< 0.5	5.50	< 3.5
RS1U	13.50	< 0.5	1.00	8.50	4.50	< 0.5	2.50	< 3.5
RS2U	18.00	1.00	1.50	10.00	5.00	1.00	3.00	< 3.5
RS3U	23.50	0.50	1.00	9.50	5.50	< 0.5	2.00	< 3.5
LS1U	4.50	1.00	0.50	8.00	5.50	< 0.5	2.50	< 3.5
LS2U	3.00	1.00	1.50	8.50	5.00	1.00	2.00	< 3.5
LS3U	3.50	0.50	1.00	7.00	4.50	< 0.5	< 2.00	< 3.5

Trace metal/metalloid in lower peeper chambers
Measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS by the Analytical Services Group at CanmetMINING. All values in µg/L.

	As	Co	Cr	Cu	Ni	Pb	Sb	Zn
BPOND1L	115800.00	2.00	1.50	6.50	12.50	< 0.5	1118.50	< 3.5
BPOND2L	112650.00	3.50	1.00	5.00	13.00	1.00	1716.00	< 3.5
BPOND3L	106100.00	2.00	1.00	3.50	13.00	< 0.5	1476.50	< 3.5
BVEG1L	1561.50	5.00	2.00	73.50	21.50	19.50	159.00	40.50
BVEG2L	2150.50	2.50	1.50	8.00	12.50	1.00	28.50	< 3.5
BVEG3L	4452.50	5.50	1.50	6.50	28.00	1.50	112.00	< 3.5
YKB1L	625.00	< 0.5	1.50	12.00	2.50	< 0.5	13.50	< 3.5
YKB2L	234.00	0.50	2.50	16.00	3.50	1.50	5.50	12.00
YKB3L	193.50	< 0.5	1.50	9.50	4.00	< 0.5	4.50	< 3.5
RS1L	27.50	1.50	1.00	19.50	17.50	< 0.5	2.00	< 3.5
RS2L	8.50	1.50	1.00	13.00	8.00	< 0.5	< 2.00	< 3.5
RS3L	37.50	2.00	1.00	23.50	16.50	1.00	3.50	< 3.5
LS1L	38.50	1.50	1.00	12.50	8.00	20.50	2.50	< 3.5
LS2L	9.50	2.00	1.00	10.00	7.00	< 0.5	< 2.00	< 3.5
LS3L	7.00	1.50	0.50	9.00	8.50	< 0.5	< 2.00	< 3.5

Appendix F – DGT Concentrations

Trace Metals, Arsenic

Trace metal DGT measurements
Measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS by the Analytical Services Group at CanmetMINING. All values in µg/L.

	Co	Cr	Cu	Mn	Pb	Zn
BPON1	0.00491	0.00578	0.19213	0.18465	0.01818	1.13801
BPON2	0.00491	< 0.00578	0.97472	0.37429	0.02181	1.35889
BPON3	0.00492	< 0.00578	1.44863	0.19471	0.05092	1.47957
BVEG1	0.00974	< 0.00573	10.24968	0.81606	0.02162	9.65074
BVEG2	0.02440	0.01148	9.07934	3.50883	0.03611	6.26581
BVEG3	0.05370	0.01148	12.13853	13.86879	0.02167	8.26974
YKB1	0.00496	0.01168	0.24140	0.06049	0.01102	0.95546
YKB2	0.00496	0.00584	0.29815	0.04536	0.00734	0.80984
YKB3	0.00496	< 0.00584	1.68493	0.06048	0.01469	1.47431
RS1	< 0.00489	< 0.00575	0.00466	0.00496	0.00361	0.02386
RS2	< 0.00484	< 0.00569	0.00461	0.00491	0.00358	0.02362
RS3	0.00489	< 0.00575	0.00466	0.00496	0.00362	0.02388
LS1	0.00492	< 0.00578	0.22036	0.11484	0.01091	0.02402
LS2	0.00656	0.01542	0.29379	0.12648	0.02425	0.03203

Trace metal DGT measurements
Low values measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS and high concentration measured by method 3VIXXX1 using an a Varian Viasta ICP-AES by the Analytical Services Group at CanmetMINING. All values in µg/L.

	As
BPON1	687.37
BPON2	572.43
BPON3	595.33
BVEG1	214.91
BVEG2	158.00
BVEG3	180.52
YKB1	7.53
YKB2	10.51
YKB3	9.53
RS1	5.48
RS2	1.60
RS3	2.69
LS1	1.73
LS2	7.69

Appendix G: Fathead Minnow Surface Water

Major Cations, Anions, Trace Metals, Arsenic Speciation, DOC

Trace metal/metaloid concentrations in fathead minnow toxicity test surface water
Measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS by the Analytical Services Group at CanmetMINING. All values in µg/L. All measurements acquired at

ppb	As	Co	Cr	Cu	Ni	Pb	Sb
BPON1	34870	< 0.1	< 0.1	1.5	2.5	< 0.3	9120
BPON2	35470	< 0.1	< 0.1	5.5	1.9	< 0.3	1140
BPON3	36660	< 0.1	< 0.1	2.5	2.2	< 0.3	1090
BVEG1	7760	0.3	1.4	27.1	4.8	< 0.3	351.2
BVEG2	9640	0.5	1.6	42.9	5.6	4	418.9
BVEG3	9890	0.3	1.7	18.6	5.1	< 0.3	514
YKB1	27.7	< 0.1	1.4	1.2	0.7	< 0.3	2.3
YKB2	34.5	< 0.1	1.5	1.4	0.5	< 0.3	2.6
YKB3	26.5	0.1	1.5	3.5	0.6	0.3	2.5
RS1	25.7	< 0.1	1.1	2.6	1.1	< 0.3	1.4
RS2	13.8	< 0.1	1.2	2.1	1.1	< 0.3	1
RS3	15.5	< 0.1	1	1.4	1.3	< 0.3	0.7
LS1	5.9	< 0.1	< 0.1	2.6	0.2	< 0.3	< 0.3
LS2	34.7	< 0.1	< 0.1	1.4	0.2	< 0.3	0.8
LS3	12.5	< 0.1	< 0.1	1.2	0.6	< 0.3	< 0.3
B2.5	7.9	< 0.1	< 0.1	2.4	0.9	< 0.3	< 0.3

Major anions in fathead minnow toxicity test surface water
Sampled by suction lysimeter, measured by method 2ICIC3 using an IonPac Analytical Column AS14 on a Dionex – ICS 160. All values in mg/L. LS and BPON measurements were taken at insertion, BVEG, RS,YKB measurements were acquired at takedown.

ppm	Cl	NO_3	PO_4	SO_4
BPON1	24	2.9	<0.9	49
BPON2	23	3.1	<0.9	51
BPON3	22	4	<0.9	46
BVEG1	58	<0.2	<0.9	54
BVEG2	51	14	<0.9	37
BVEG3	50	14	2.18	42
YKB1	43	21	<0.9	32
YKB2	43	21	<0.9	32
YKB3	45	27	<0.9	41
RS1	39	30	<0.9	27
RS2	33	12	<0.9	26
RS3	39	19	<0.9	26
B2.5	34	17	<0.9	27
LS1	8	<0.2	<0.9	8.8
LS2	9.9	1.7	<0.9	12
LS3	9.6	0.8	<0.9	12

Arsenic speciation in fathead minnow toxicity test surface water
Measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS by the Analytical Services Group at CanmetMINING. All values in µg/L. LS and BPON measurements were taken at insertion, BVEG, RS,YKB measurements were acquired at takedown.

	As(III)	As(V)
BPON1	< 5.0	37890
BPON2	< 5.0	38400
BPON3	< 5.0	37760
BVEG1	4.7	1126
BVEG2	9	1226
BVEG3	5.4	918.9
YKB1	< 0.5	29.4
YKB2	0.8	34.4
YKB3	28.8	7.7
LS1	0.6	3.2
LS2	1	22.9
LS3	< 0.5	7.5
RS1	0.9	8.7
RS2	< 0.5	5.8
RS3	1	17.4

Dissolved organic carbon in fathead minnow toxicity test surface water
Measured by the Analytical Services Group at CanmetMINING. All values in mg/L. LS and BPON measurements were taken at insertion, BVEG, RS,YKB measurements were acquired at takedown.

	DOC
BPON1	<0.1
BPON2	13.5
BPON3	9.3
BVEG1	20.2
BVEG2	14.4
BVEG3	15.8
YKB1	13.3
YKB2	10.7
YKB3	11.5
RS1	13.7
RS2	11.8
RS3	13.4
LS1	7.7
LS2	9.6
LS3	8

Abstract H: Sequential Extractions

Trace Metals, Arsenic

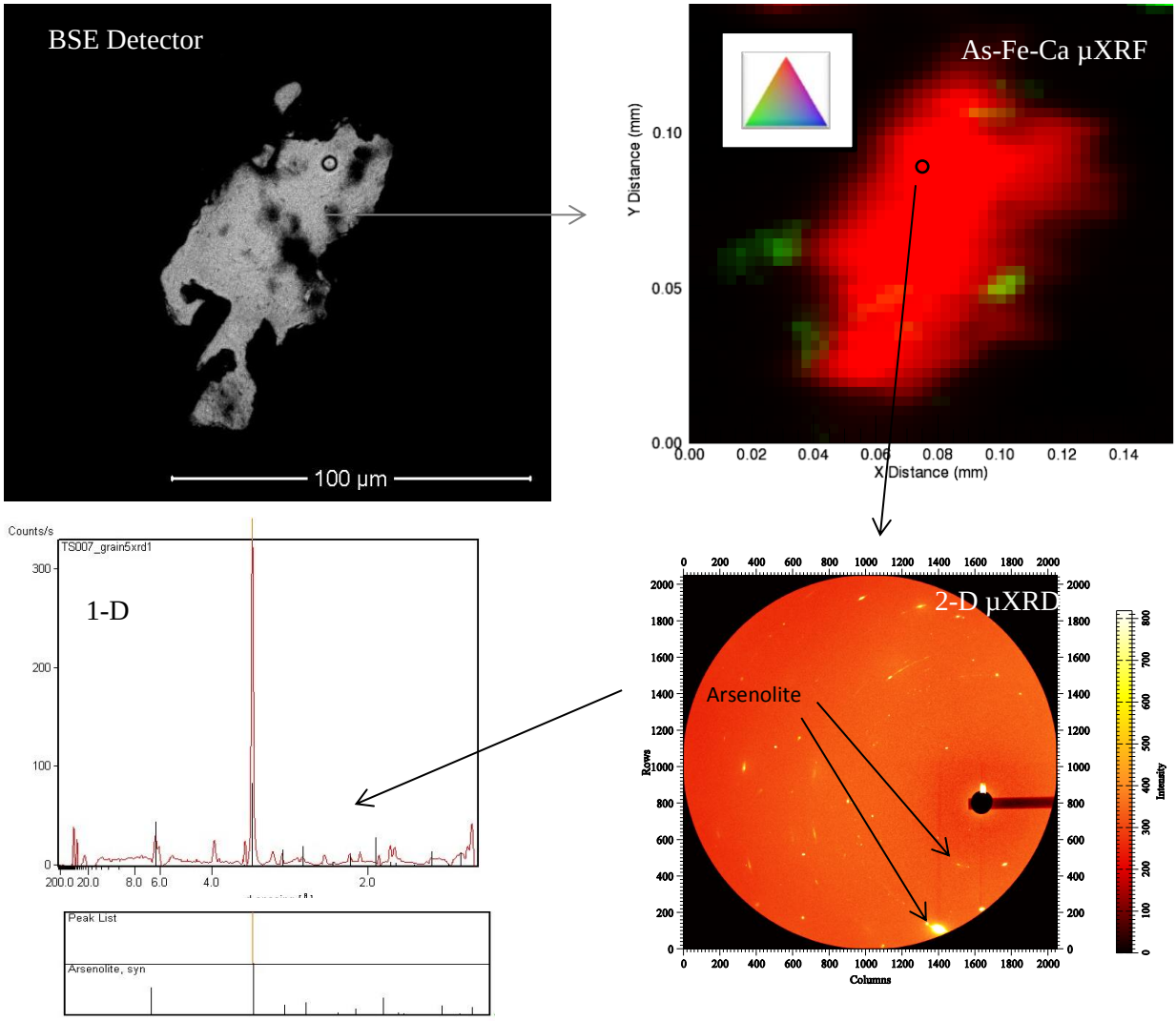
Trace metal/metalloid in BCR sequential extractions
Measured by method 3MSXX2 using an ELAN 6100 – DRC (dynamic reaction cell) ICP-MS by the Analytical Services Group at CanmetMINING. All values in mg/kg.

	As	Co	Cr	Cu	Ni	Pb	Sb	Zn
Ex./Acid Sol. YKB	4.43	1.92	0.33	2.10	1.53	0.10	< 0.06	5.60
Reducible YKB	9.07	1.35	0.62	5.29	1.82	1.17	< 0.06	6.09
Oxidizable YKB	4.61	1.93	2.90	3.24	4.24	1.58	< 0.07	6.46
YKB Total	18.11	5.21	3.85	10.64	7.59	2.85	0.18	18.15
Ex./Acid Sol. BOVEG	232.80	7.43	0.41	37.45	25.03	4.14	12.77	196.27
Reducible BOVEG	177.33	4.66	3.23	189.07	19.70	23.19	6.74	171.73
Oxidizable BOVEG	2077.12	8.09	10.44	820.80	25.57	84.69	47.75	195.52
BOVEG Total	2487.25	20.19	14.07	1047.32	70.30	112.03	67.26	563.52
Ex./Acid Sol. BPON	3751.47	2.32	0.47	1.40	5.33	0.03	22.50	18.31
Reducible BPON	3203.47	1.78	2.34	5.71	5.24	2.19	15.12	20.24
Oxidizable BPON	3684.80	1.07	6.18	9.36	3.46	2.26	31.76	10.37
BPON Total	10639.73	5.17	8.99	16.47	14.03	4.48	69.38	48.92
Ex./Acid Sol. Blank	0.10	0.003	0.27	0.07	0.03	0.01	< 0.06	0.11
Reducible Blank	18.85	0.005	0.05	0.04	0.06	0.01	< 0.06	0.49
Oxidizable Blank	1.38	0.01	0.66	0.36	0.09	0.08	< 0.07	0.55
Ex./Acid Sol. BCR701	2.44	2.41	3.84	72.37	17.72	6.44	0.10	220.80
Reducible BCR701	18.95	2.20	16.82	95.20	15.02	70.92	< 0.07	73.60
Oxidizable BCR701	11.50	1.64	145.60	63.16	16.22	28.58	0.12	45.31

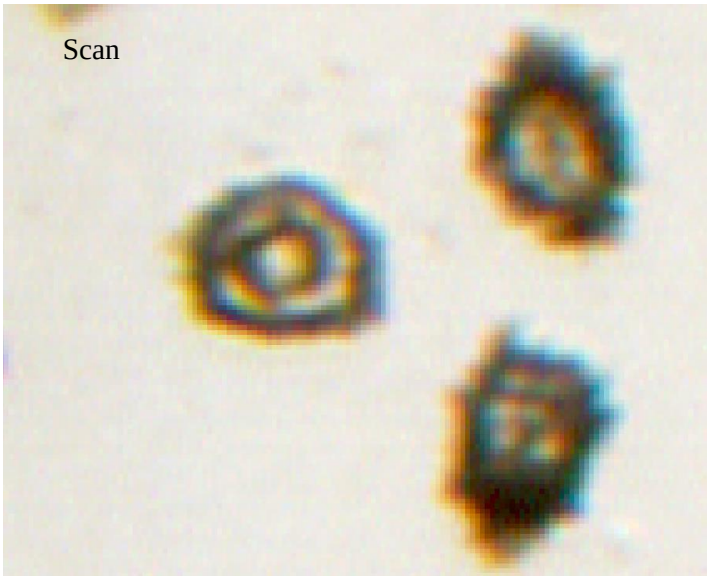
Abstract I: ESEM and Synchrotron Target Identification

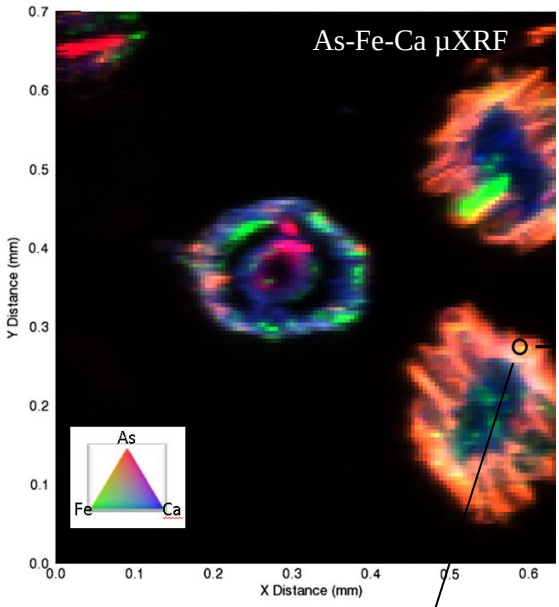
Abstract I contains examples of ESEM and synchrotron methods results used for target identification. The rest of the target identifications are available upon request in CD format as is additional raw data.

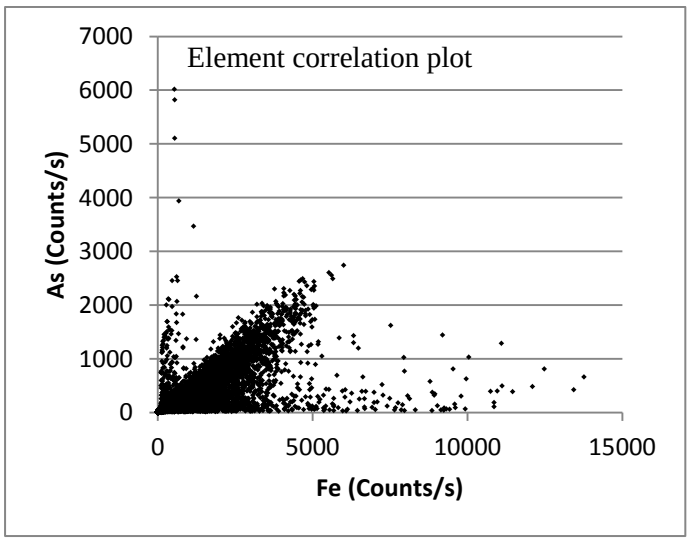
Baker Outlet TS007 grain five arsenolite identification. BSE was used to locate the grain and uXRF was used to re-map the grain at synchrotron facilities. uXRD was used to confirm the arsenolite identification. uXANES could not be used because of self-adsorption caused by the high As concentration.

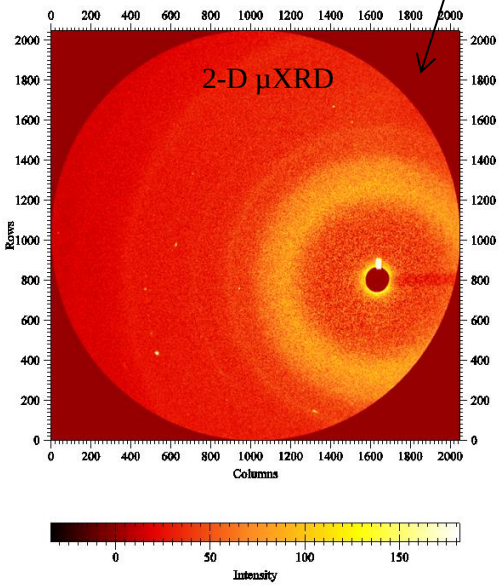


Baker Vegetated root 1 root-plaque identification. Flatbed scanner image of roots show the true color of the roots. A false color uXRF scan shows As-Fe overlap. uXRD shows the amorphous nature of the material. Element correlation plot shows the Fe concentration controls the As concentration.

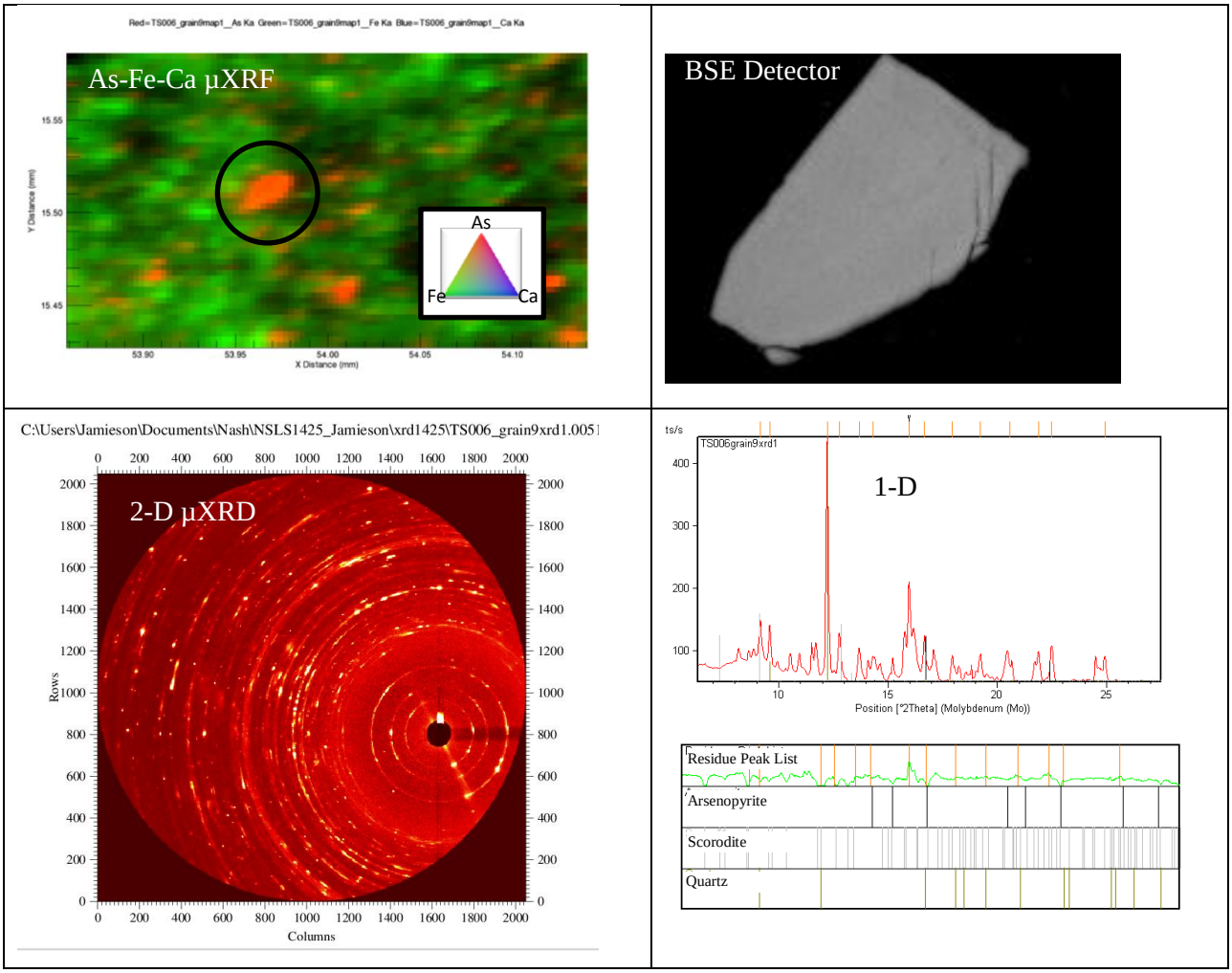








Yellowknife Beach Grain 9 identification. Flatbed scanner image of roots show the true color of the roots. A false color uXRF scan shows As-Fe overlap. uXRD shows the amorphous nature of the material. Element correlation plot shows the Fe concentration controls the As concentration.



Abstract J: Raw Data

Abstract J contains all of the raw geochemical data, labelled, used for the thesis. It is available upon request in CD format.