A Study of Arsenic Contamination From the Royal Oak Giant Mine, Yellowknife, Northwest Territories

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A STUDY OF ARSENIC CONTAMINATION FROM THE ROYAL OAK GIANT MINE, YELLOWKNIFE, NORTHWEST TERRITORIES

By

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ABSTRACT

Arsenic is a naturally occurring element found within the earth's crust. It has been used as a poison and for medicinal purposes. The current major use of arsenic is as chromated copper arsenate for the treatment of pressure treated wood. In Canada, the major anthropogenic discharges to the environment are aerial emissions from smelters and runoff from mine tailings produced by gold mines.

The toxicity of arsenic is dependent on the oxidation state and the species. Various forms are known to have mutagenic, reproductive and carcinogenic effects in humans, and cause chronic poisoning. Arsenic and its inorganic compounds are considered toxic as defined by section 11 of the *Canadian Environmental Protection Act* (CEPA).

The Royal Oak Giant Mine, situated 5 km north of the City of Yellowknife in the Northwest Territories, has been mining gold since 1948. The waste streams from mining operations include tailings, effluent and aerial emissions. During the first 5 years of operations prior to the construction of a series of four tailings ponds, the tailings were deposited on the shore of Yellowknife Bay. The effluent from these tailings ponds is discharged into Baker Creek, which empties into Yellowknife Bay. In 1981, the effluent discharge treatment plant became operational and reduced the quantities of contaminants being discharged into the environment. Concern persists, however, regarding the environmental impact of the mining activities.

A number of studies have been conducted in the Yellowknife area, but none have determined the overall amount of anthropogenic arsenic, investigated the cycling of arsenic, or sampled from Baker Creek and the Tailings ponds. Samples for the work described in this thesis were obtained during two one-week sampling periods starting 22 June and 23 August 1997. Samples included tailings, grab samples, sediment cores, porewater and surface water samples.

A method for arsenic analysis of sediment and tailings was developed using the TN Spectrace 9000 X-Ray Fluorescence (XRF). The XRF proved to be very effective and may facilitate arsenic analyses at heavily contaminated sites.

It was found that Baker Creek and its outlet into Yellowknife Bay contain surface sediment concentrations of arsenic ranging from 1193 ppm to 3821 ppm. However, the background arsenic concentration within Baker Creek and Yellowknife Bay was determined to range from 41 to 104 ppm and 7 to 25 ppm, respectively.

It was determined that the tailings previously deposited onto the shoreline (the Beach Area) is eroding and presently cover an area of approximately 16 ha within the Bay. The arsenic load was estimated to be 41 400, 12, 51 and 44 tonnes of arsenic in the tailings ponds, Baker Creek, Yellowknife Bay and the Beach Tailings Area, respectively.

A standard sequential extraction tests was used to determine the amount of arsenic in the various solid phases. Leachate tests were conducted to investigate the availability of the arsenic. The majority of the arsenic in the tailings (69% or 2120 ppm) is found within the residual phase with the remainder (31% or 970 ppm) in the more available phases. The majority of the arsenic (67% or 1420 ppm) in the sediments is found in the more available manganese and iron oxides phase. A leachate test demonstrated that the arsenic within the sediments is more available than the arsenic in the tailings.

Anthropogenic activities are the primary sources of contaminants in the study area. Dissolved arsenic from the effluent discharge is the primary form, followed by particulate, aerial and natural. The levels of contaminants at the various sample locations demonstrated that the effluent discharge is the primary source of contaminants in the study area. The discharged arsenic would appear to be in the dissolved form, as confirmed by the predominance of arsenic bound to the iron and manganese oxide phase.

Porewater concentrations up to 3371 ppb (Yellowknife Bay) were determined and demonstrated the availability of the arsenic to the environment due to the calculated upward arsenic diffusive flux ranging from 0.6 to 26.9 $\mu g\ cm^{-2}\ y^{-1}$.

The anthropogenic loading of arsenic and its potential for redistribution has been determined in the study area. Toxicological studies are required before any final decisions can be made on what is necessary for reclamation. However, estimates have been made of the costs of various reclamation options.

Dredging of the sediments with disposal in the tailings ponds is an option for the heavily contaminated sediments in Yellowknife Bay and the Beach Area at an estimated cost of $978 000. The cost for the removal of the Baker Creek sediments has not been determined. The tailings will not be a source of future contamination if they are isolated from wind erosion, water erosion and leaching into the groundwater. Possible solutions

include covering the ponds with an impervious membrane ($11 400 000 to $14 900 000) or a simple 20 cm layer of gravel ($2 700 000).

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I. INTRODUCTION

The City of Yellowknife, Northwest Territories is situated on the western shore of Yellowknife Bay, which is located on the northern shore of Great Slave Lake. The Royal Oak Giant Mine, 5 km north of the City of Yellowknife, has been mining gold continuously since 1948. The mine currently employs approximately 280 people and plays a important role in the local economy.

The byproducts from the mining operations include tailings, effluent and aerial emissions. The waste streams contain elevated levels of arsenic as the concentration of arsenic within the gold bearing ore is high. The effluent is treated prior to discharge into Baker Creek, which flows for 3 km before emptying into Yellowknife Bay.

The residents of the City of Yellowknife and the native communities of Dettah and in Ndilo have expressed concern over the high levels of arsenic found in the area. Yellowknife Bay is used for various water sports, fishing and as a secondary source of drinking water. Any contamination of the local environment could possibly have a direct effect on the inhabitants of the city.

It is accepted that arsenic can have carcinogenic and mutagenic effects, not to mention chronic poisoning, for humans (Morton and Dunnette, 1994); negative effects are also apparent in other organisms at elevated concentrations (Naqvi, 1994). Arsenic and its inorganic compounds is considered to be toxic under section 11 of the *Canadian Environmental Protection Act* (CEPA). It should be noted, however, that the toxicity of arsenic varies greatly with the chemical form or species as some forms have no effect on humans.

Three previous studies have examined the concentrations of arsenic in water and sediments in various sections of Yellowknife Bay (Mudroch *et al.*, 1989; Sutherland, 1989; Jackson *et al.*, 1996). However, no study to date has covered the entire area affected by the operations of the mine, including the tailings ponds, Baker Creek and Yellowknife Bay.

The field portion of this study was conducted over two one-week periods in June and August 1997. Logistical support in Yellowknife was provided by Environment Canada. The samples were collected by personnel of the Environmental Sciences Group

(ESG) of the Royal Military College (RMC), the University of British Columbia and the Environment Canada office in Yellowknife.

The specific goals of the work reported in this thesis are:

- A method application for arsenic analysis of sediment and tailings.
- A determination of the natural, background, concentration of arsenic in the study area.
- An estimation of the overall extent of arsenic contamination due to the operations of the Giant Mine.
- An initial evaluation of the stability and bioavailability of the arsenic.
- An evaluation of the cost of possible reclamation options.

II. ARSENIC

A. Sources of arsenic

Arsenic is a naturally occurring element which ranks 20th in terms of abundance in the earth's crust. It has been estimated that the natural weathering of arsenic containing rocks contributes 40 000 tonnes of arsenic per yr. to the environment (Eisler, 1994). Within the Canadian environment, background levels of arsenic are reported to range from 4.8 to 13.6 ppm for soil, <20 ppm for sediment, <2 ppb in surface water and <50 ppb in groundwater (CEPA, 1993).

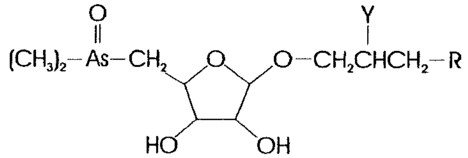
The two main sources of anthropogenic arsenic contamination in Canada are aerial emissions from smelters and runoff from mine tailings produced by gold mines. Other sources include power stations which use coal or fossil-fuels as their energy source, and locations where arsenic based pesticides are used (Eisler, 1994). The amount of arsenic introduced into the Canadian environment per year is estimated to be 15 tonnes of liquid effluent from base-metal smelters and refineries, 310 tonnes in aerial transmissions and 770 tonnes of solid wastes disposed on land (CEPA, 1993).

B. Forms of Arsenic

In the environment, arsenic is commonly present in two oxidation states, III and V. The positive polarization of arsenic is obvious with respect to various elements (C, O and S) due to the prominent differences in electronegativity. However, with respect to hydrogen, the difference is not as distinct. The electronegativities, as determined by Pauling and Allred-Rochow, for arsenic are estimated to be 2.18 and 2.20. For hydrogen, they are 2.1 and 2.20. In a review by Cullen and Reimer (1989), arsenic was assumed to be the more electropositive element to reduce confusion.

Table II-1 presents a summary of the various forms of arsenic found within the environment. The inorganic arsenicals (arsenite and arsenate) are the most commonly found forms within the freshwater environment. They are generally referred to as As(III) and As(V), respectively, even though there are other arsenic species in these oxidation states (such as $^{+}5$ state found in the methylated species) (Cullen and Reimer, 1989).

Table II-1: Chemicals forms of various arsenic compounds (Anderson and Bruland, 1991; Yamauchi, 1994).

Name	Abbreviation	Chemical Formula
	Inorganic Arsenic	
Arsenite	As(III)	As_2O_3 (s) $As(OH)_3$ (aq)
Arsenate	As(V)	As_2O_5 (s) H_3AsO_4 (aq)
Arsine		AsH_3
	Organic Arsenic	
Monomethylarsonic acid	MMAA	$CH_3AsO(OH)_2$
Dimethylarsinic acid	DMAA	$CH_3)_3AsOOH$
Trimethylarsine	TMA	$(CH_3)_3As$
Trimethylarsine oxide	TMAO	$(CH_3)_3AsO$
Arsenobetaine	AB	$(CH_3)_3As^+CH_2COO^-$
Arsenocholine	AC	$(CH_3)_3As^+CH_2CH_2OH$
Arsenosugars	Sugar X-XIV	

*The degree of protonation of the arsenic acids is pH dependent.

The methylated species (MMAA, DMAA and TMA) have been detected at small levels (< 1 ppb) in the surface water and porewater of lakes influenced by the effluent from the Con Mine in Yellowknife (Bright *et al.*, 1996) and in various freshwater organisms (Maeda, 1994). They are also present in the marine environment in surface water (Francesconi and Edmonds, 1994), in porewater (Reimer and Thompson, 1988) and in marine plants (Cullen and Reimer, 1989).

The majority of the arsenic found in marine organisms is in the organic form. Arsenosugars have been found in algae, and arsenobetaine and arsenocholine are found in fish, molluscs, and crustaceans (Maeda, 1994).

C. Uses

Arsenic has been used for a variety of medicinal and other purposes since 400 BC. During the middle ages, arsenic, as arsenite, was the "preferred homicidal and suicidal agent". In contrast, both inorganic and organic arsenicals were commonly used to treat a variety of illnesses, including syphilis, yaws, and trypanosomiasis up until 1945 when better drugs (i.e. penicillin) were developed. Arsenical drugs are still used today for the treatment of African sleeping sickness and amoebic dysentery (Eisler, 1994).

Worldwide, the annual production of arsenic trioxide (As (III)) is between 50 000 and 53 000 tonnes. The major use of arsenic trioxide is as a wood preservative for the production of pressure treated lumber. Chromated copper arsenate (47.5% CrO_3, 18.5% CuO, and 34% As_2O_3) has come into favour as the replacement chemical for creosote. A secondary use of organic arsenic is as a herbicide, an insecticide, an algaecide, a plant desiccant and as a defoliant, especially in the cotton industry. Arsenic is also used in the manufacturing of glass to reduce air bubbles, in non-ferrous alloys, and in the electronics industry in the form of pure arsenic metal in semiconductors (Ishiguro, 1992). The two major uses for arsenic within Canada are wood preservatives and metallurgical applications (CCME, 1997).

D. Toxicity of Arsenic

The speciation or chemical form of arsenic will determine its toxicity, but impact will be affected by the mode of uptake and subsequent metabolism. Some general points can be considered when assessing the toxicity of arsenic (Eisler, 1994):

1. Arsenic absorption occurs by inhalation, ingestion and dermal contact.

2. The method of arsenic absorption by cells is similar to that of phosphate transport.

3. After absorption, most arsenicals are excreted in urine within a week.

4. The order of arsenic toxicity, from most toxic to least toxic is as follows:

arsines>inorganic arsenites>organic trivalent compounds>inorganic arsenates>organic pentavalent compounds>arsonium compounds>elemental arsenic

5. The toxicity of arsenic increases with increased solubility.

These factors have important effects on the LD_{50} (the lethal dose required for 50% of test animals) (Table II-2).

Table II-2: A comparison of the LD_{50} in animals for various arsenic compounds (Yamauchi, 1994)

Arsenic Compound	Chemical Formula	LD_{50} (mg/kg)	Animal/Mode of Administration
Arsenite: arsenic trioxide	As_2O_3	34.5	Mouse / oral
Arsenite: sodium arsenite	$NaAsO_2$	4.5	Rat / intraperitoneal
Arsenate: sodium arsenate	Na_2AsO_4	14-18	Rat / intraperitoneal
MMAA: monomethylarsonic acid	$CH_3AsO(OH)_2$	1800	Mouse / oral
DMAA: dimethylarsinic acid	$(CH_3)_3AsOOH$	1200	Mouse / oral
TMA: trimethylarsine	$As(CH_3)_3$	10 000	Mouse / oral
TMAO: trimethylarsine oxide	$(CH_3)_3AsO$	10 600	Mouse / oral
Arsenobetaine	$(CH_3)_3As^+CH_2COO^-$	8000	Mouse / subcutaneous
TDAA: trisdimethylaminoarsine	$As[N(CH_3)_2]_3$	15	Mouse / subcutaneous

Arsine gas is considered the most toxic form of arsenic (Eisler, 1994). It has a boiling point of −55°C (Francesconi *et al.*, 1994) and is a colourless, nonirritating gas. Inhalation results in the rapid destruction of the red blood cells, possibly followed by kidney failure and, without proper therapy, death (Gorby, 1994).

1. *Arsenic Toxicity and Humans*

Inhalation and/or ingestion are the primary modes of absorption by humans, although trivalent arsenic can be absorbed through the skin. Ingested arsenic remains in the body for a shorter period of time than inhaled arsenic due to its rapid biotransformation by the liver. The primary reaction to the absorption of arsenic is gastrointestinal irritation for ingested arsenic and respiratory irritation for inhaled arsenic (Morton and Dunnette, 1994). The detoxification process consists of the reduction of arsenates to arsenite, followed by methylation. The methylated species are then readily excreted from the body through the urine (Eisler, 1994)

The symptoms for chronic poisoning can include weakness, fatigue, absence of motivation, anorexia and hair loss. However, many of these symptoms are not specific to arsenic. Arsenic is also known to have mutagenic, reproductive and carcinogenic effects

(Morton and Dunnette, 1994). More complex organoarsenicals, such as arsenobetaine, are not metabolized and pass through the body unchanged.

As a mutagen, arsenic has been shown to have effects ranging from simple gene mutations to visible changes in the chromosome structure, with arsenite being more potent than arsenate. This effect is likely due to the inhibition of DNA repair, as opposed to by direct gene damage. It is thought that these changes may be passed on to subsequent generations (Morton and Dunnette, 1994).

It is known that inorganic arsenic compounds can cross the placental barrier and have adverse effects on fetal development. Organic arsenicals do not have these effects. In the region of the Ronnskar smelter in Sweden, women employed at the smelter delivered babies with reduced birth weights and there were increases in the rate of spontaneous abortions and congenital malformations. In Massachusetts, the rate of spontaneous abortions was found to increase by a factor of 1.7 for women consuming water with high arsenic levels, 1.4 - 1.9 ppm (Morton and Dunnette, 1994).

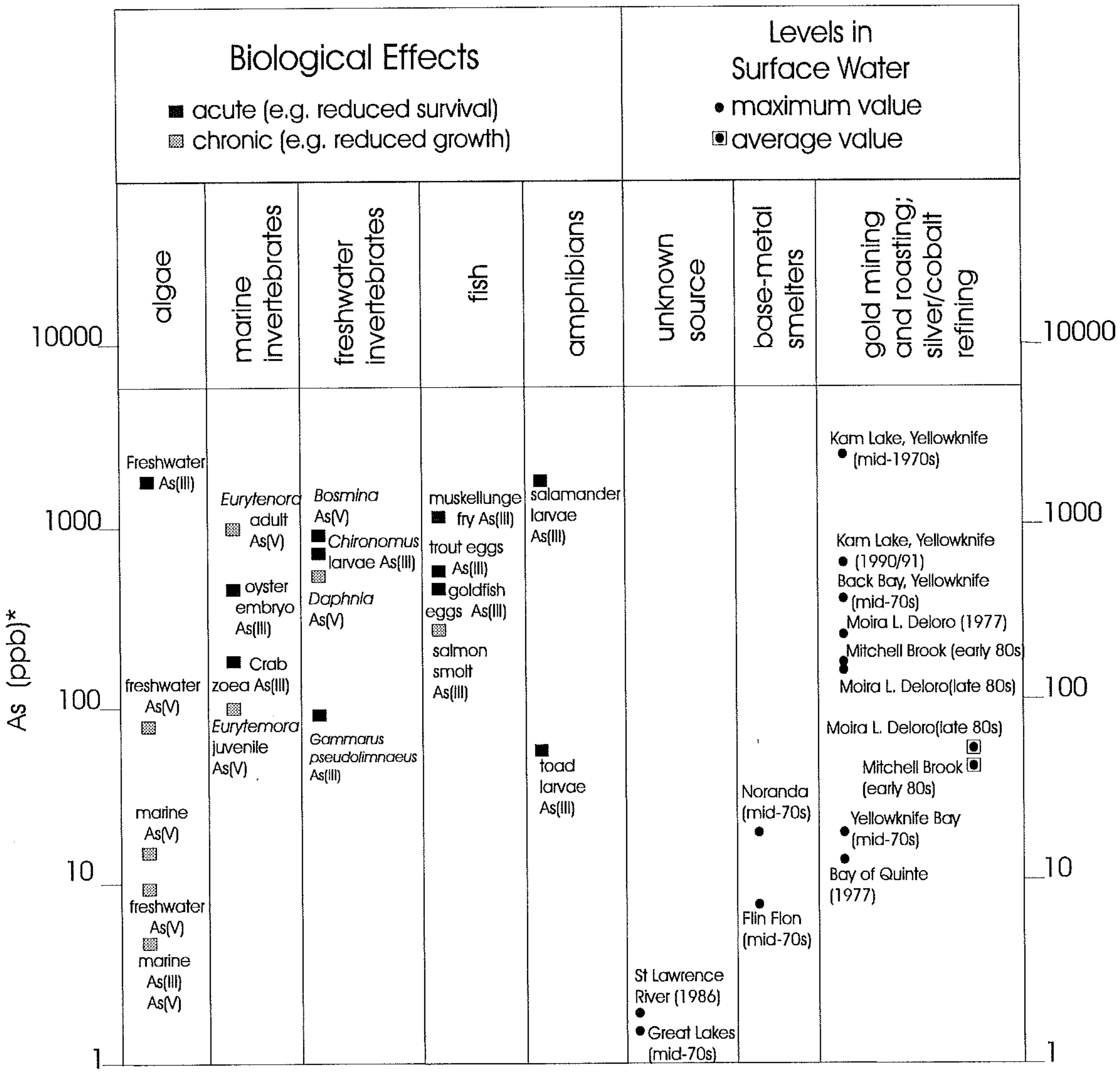
The carcinogenic effect of arsenic is as a promoter as opposed to an initiator. The carcinogenic risk declines with time once exposure has ceased. Separate studies were conducted at the Tacoma copper smelter in Washington, the Anaconda smelter in Montana and the Ronnskar smelter in Sweden; all of these provide significant evidence of the ability of arsenic to induce lung cancer. The increase in risk was shown to be a function of duration of exposure and concentration (CEPA, 1993).

High levels of arsenic in drinking water result in the accumulation of arsenic in the skin and subsequent increases in skin cancer rates. The residents of a town in Chile, where arsenic levels ranged from 0.05 to 0.95 ppm (mean 0.6 ppm), were found to have higher levels of skin cancer. In southwestern Taiwan, drinking water obtained from wells was found to have arsenic from 0.01 to 1.82 ppm (mean 0.5 ppm). A number of studies showed that skin cancer rates increased directly with increased arsenic concentration in water and duration of intake. In the same area, higher rates of colon, bladder, renal, lung and liver cancer have also been observed (Morton and Dunnette, 1994).

2. *Arsenic Toxicity in the Environment*

Within the natural environment, arsenic is bioaccumulated by organisms, but not biomagnified through the food chain (Eisler, 1994). It is believed that animals are more resistant to arsenic than humans due to differences in gastrointestinal absorption. However, among mammals, there are significant differences between species. Hamsters have been shown to have low gastrointestinal absorption, rats are affected by excessive binding to red blood cells, and marmoset monkeys have low methylating capabilities. These make it difficult to relate information obtained from other mammals directly to humans (Naqvi, 1994).

Summaries of arsenic levels found in Canadian surface waters and sediments are shown in Figure II-1 and Figure II-2. The known total arsenic levels are compared with a summary of observed biological effects for As (III) species, primarily H_3AsO_3 (arsenite) and As(V) species, principally $HAsO_4^{-2}$ and $H_2AsO_4^-$ (arsenate).



* dry weight; typically or strong acid-extractable

Figure II-1: Arsenic concentrations in Canadian surface waters and the biological effects at corresponding levels of exposure [adapted from (CEPA, 1997; Eisler, 1994)].

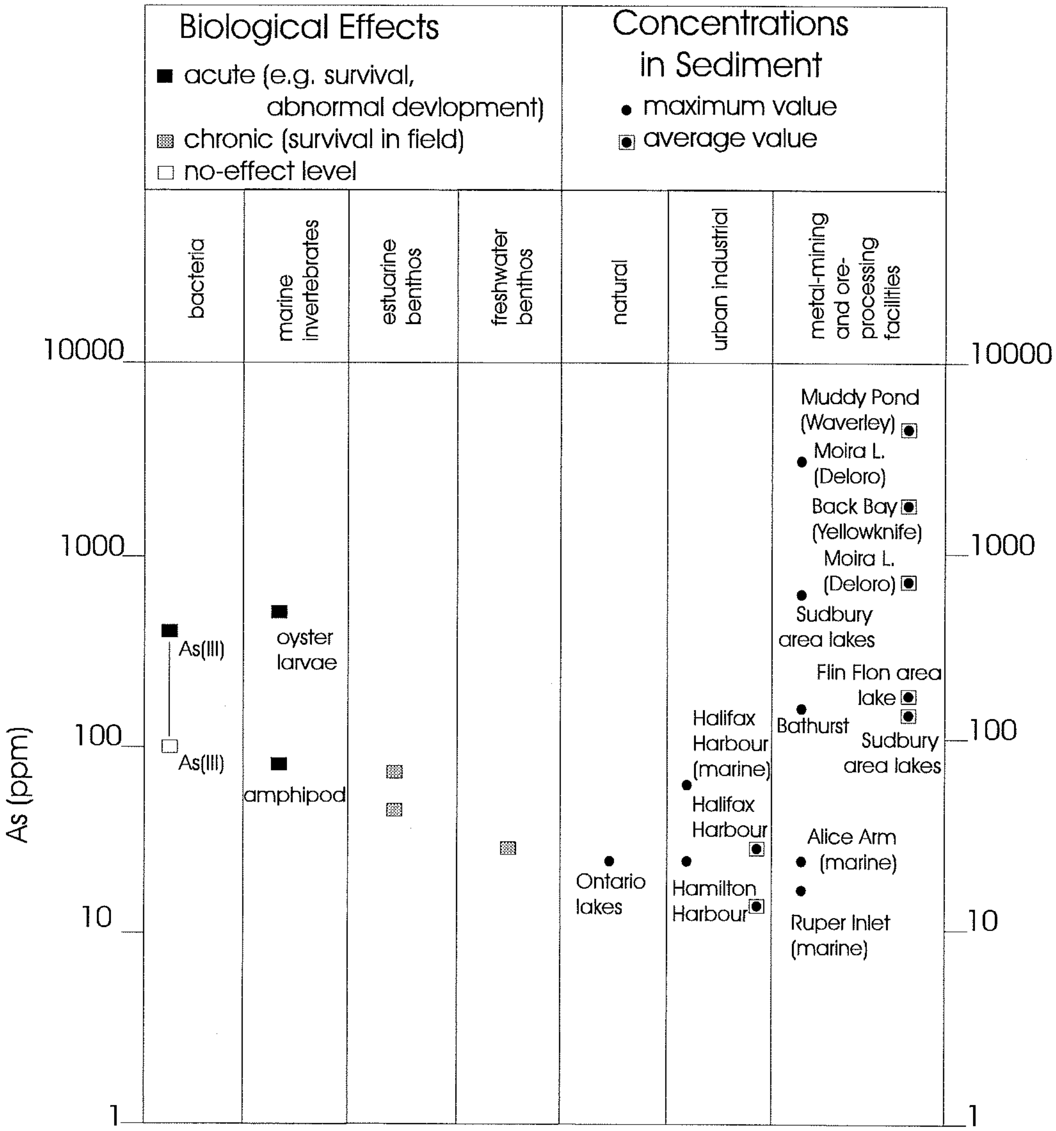


Figure II-2: Arsenic concentrations in Canadian sediments and biological effects at corresponding levels of exposure [adapted from (CEPA, 1997)]

E. Arsenic in the Environment

1. Geochemical cycle of arsenic

Arsenic undergoes a number of changes in response to environmental conditions such as pH and redox potential. These factors are important as they will determine the fate and biological availability of the arsenic in mine tailings, effluent discharge and affected sediments. Several models have been proposed for the geochemical cycling of arsenic. Figure II-3 represents a consolidation of prevailing theories for inorganic arsenic. The behaviour of organic arsenicals is less well understood. The following sections expand on the features of this model.

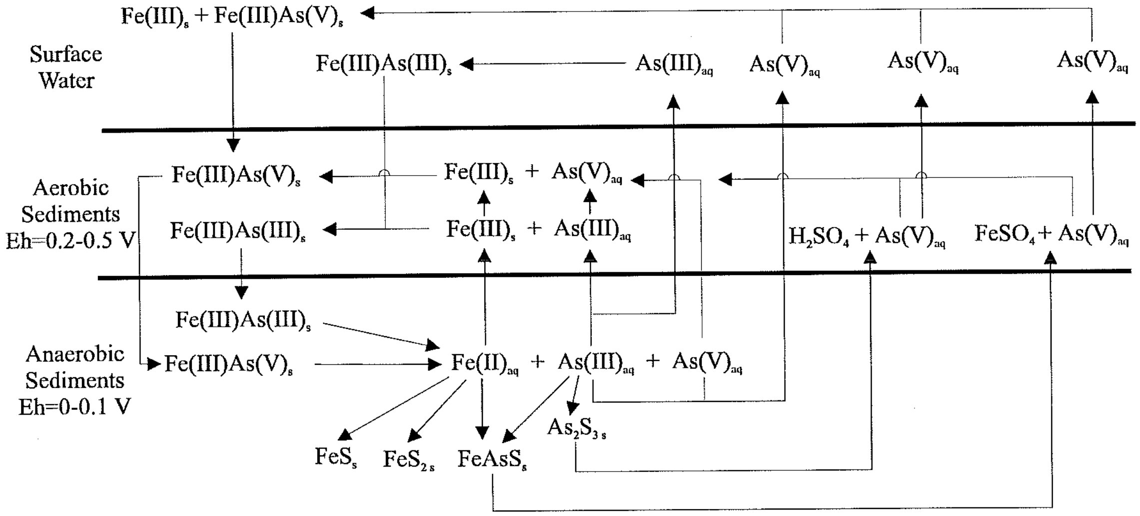


Figure II-3: The geochemical cycle of arsenic in natural waters (adapted from Aggett and O'Brien, 1985; Moore *et al.*, 1988; Cullen and Reimer, 1989; Mok and Wai, 1994).

2. Factors Affecting the Oxidation State

The oxidation state of arsenic within the environment is affected by the pH, redox conditions (Mok and Wai, 1994) and by transformations caused by microorganisms (Cullen and Reimer, 1989). The As(III)/As(V) ratio, as well as the relative proportions of dissolved and solid phase arsenic, is dependent on a combination of the various factors.

At normal pH levels (5-8), redox conditions primarily control the As(III)/As(V) ratio. As(V) is the major species in oxic conditions (Eh = 0.2 – 0.5 V) and has low solubility. The arsenic solubility increases and As(III) becomes the major species in anoxic conditions (Eh = 0 – 0.1 V) (Mok and Wai, 1994).

The solubility of arsenic increases at both ends of the pH scale. At low pH, the iron and manganese oxides dissolve and simultaneously release arsenic. At high pH, the arsenic sorbed to metal hydroxides can be replaced by the increased number of hydroxides (Mok and Wai, 1994).

The oxidizing and reducing capabilities of a number of strains of bacteria have been identified. The oxidizing mechanism is considered a protective mechanisms as As(V) is less toxic than As(III). Due to microbial action, the ratios found in the environment are rarely equivalent to the thermodynamically determined ratios (Cullen and Reimer, 1989).

3. *Iron Hydroxides*

Dissolved arsenic is predominantly in the As(V) form within an oxygenated water column. Arsenic accumulates in sediments primarily by the adsorption on and co-precipitation with hydrous iron oxides. Iron is generally present as Fe^{+3} (i.e. Fe(III)) in oxic conditions and Fe^{+2} (i.e. Fe(II)) in anoxic conditions. Additionally, the mineral scorodite can formed, as proposed by equation 1 (Mok and Wai, 1994).

$$(1)\ Fe(OH)_3 + H_3AsO_4 = FeAsO_4{\cdot}2H_2O + H_2O$$

These mechanisms can explain the higher arsenic levels in the sediment vs. water (Ahmann *et al.*, 1997). As the sediments are buried, they become increasingly anoxic due to consumption of oxygen by the benthic community (Wetzel, 1983). This leads to the reduction of iron oxides and arsenate to the more soluble forms of Fe(II) and As(III). It has been shown that micro-organisms can have direct and indirect roles in this reduction process. Certain types of bacteria are known to be iron-reducing in anoxic conditions. This leads to an increase in the amount of arsenic dissolution from the sediments and the reduction of arsenate to arsenite (Ahmann *et al.*, 1997; Aurillo *et al.*, 1994).

The arsenite and arsenate can diffuse upwards upon reduction and dissolution. This results in at least partial readsorption to and/or co-precipitation with iron oxides upon reaching oxic sediments with the rate of adsorption of arsenate being higher. Only partial readsorption will occur as both arsenate and arsenite are more soluble than the iron oxides. This will allow for the redistribution of arsenic into the water column even when the top layer of sediment is aerobic (Cullen and Reimer, 1989).

If the anoxic zone continues through the sediments into the water column, the rate of arsenic redistribution will be greater than when there is an aerobic layer of sediments (Belzile and Tessier, 1990). This was demonstrated by a study on arsenic in a lake in New Zealand by Aggett and Kriegman (1988). It was found that the concentration of arsenic, primarily arsenite, at the sediment/water interface during anoxic conditions was 10 times greater than that of oxygenated water. In general, the rate of oxidation of arsenite is increased by chemical oxidation with manganese and iron oxyhydroxides (CEPA, 1993), by the presence of certain bacteria and increased light exposure, initial arsenite concentration, temperature and salinity (Cullen and Reimer, 1989).

The covering of arsenic contaminated sediments with clean sediments will not necessarily isolate arsenic from entering the top sediment layer or the water column. As the contaminated sediments become anoxic, the possibility exists that upward diffusion of the arsenic into the overlying sediment and water column will occur. Therefore, simply covering contaminated sediments may not prevent further redistribution of contaminants (Azcue and Nriagu, 1994).

Arsenic is capable of diffusing into the overlying water column when oxic conditions persist in the top sediment layer and in the water column. It will, however, occur at a lesser rate than when anoxic conditions exists. The rate of diffusion will be affected by the thickness of the oxic sediments, the permeability of the sediments and the hydraulic gradient. Incomplete adsorption and co-precipitation of the arsenic with the iron oxides may occur in cases where a thin oxic layer exists (Cullen and Reimer, 1989). This natural cycling of arsenic allows for two possible modes of redistribution of arsenic, either by redistribution of sediments through bulk movement or dissolution from sediments into the water column (Bright *et al.*, 1994).

4. Manganese Hydroxides

Manganese hydroxides are similar to iron hydroxides in their relationship with arsenic in that they co-precipitate out of the water column with iron hydroxides and arsenic followed by sorption. Under reducing conditions, the Mn(IV) is reduced to Mn(II) allowing for the release of the arsenic. Manganese is not considered a major factor in the cycling of arsenic because it will dissolve prior to iron in reducing conditions. The release of arsenic can then be reversed by readsorption on iron oxyhydroxides. Upon entering oxic conditions, manganese will remain dissolved longer than does the iron (Azcue and Nriagu, 1994). Manganese oxides have a net negative surface charge under natural water pH, which is not conducive to the sorption of arsenic because it is anionic in the dissolved state. However, the adsorption of divalent cations can change surface charge of the manganese oxide (Mok and Wai, 1994). Equations 3 and 4 show the proposed reactions for the oxidation of arsenite to arsenate (Belzile and Tessier, 1990) and the co-precipitation of arsenic with hydrous manganese oxides (Masscheleyn *et al.*, 1991).

(2) $MnO_{2(s)} + H_3AsO_3 = Mn^{2+} + HAsO_4^{2-} + H_2O$

(3) $3MnOOH + 2HAsO_4^{2-} + 7H^+ + 3e^- = Mn_3(AsO_4)_2 + 6H_2O$

5. *Sulfidic Sediments*

Sulfides in anoxic sediments will scavenge the arsenic mobilized from the hydrous oxides. As opposed to diffusing upwards to the oxic layer, sulfides scavenge the dissolved arsenic and form arsenic sulfide precipitates. It is suggested that the sulfides play a role in the reduction of arsenate to arsenite, equations 4-6 (Mok and Wai, 1994; Ahmann *et al.*, 1997).

(4) $H_2AsO_4^- + 3H^+ + 2e^- = H_3AsO_3 + H_2O$

(5) $2H_3AsO_3 + 6H^+ + 3S^{2-} = As_2S_3\ (s) + 6H_2O$

(6) $2As_2S_3 + 4e^- = 4AsS\ (s) + 2S^{2-}$

If these sediments remain anoxic, they can be the ultimate sink for arsenic. However, if the sediments become oxygenated, the sulfides are oxidized and form soluble SO_4^{2-} and H^+, with the arsenic being released. If this occurs, the arsenic previously bound to the sulfides can become a source of secondary arsenic contamination (Moore *et al.*, 1988). In the presence of high concentrations of S^{2-}, soluble arsenic may be released as AsS_3^{3-}; this chemistry is not well understood but may play a major role in anoxic environments (Cullen and Reimer, 1989).

6. Biotransformation

As previously stated, biotransformation has an effect on the oxidation and reduction of arsenic within the water column and sediments. Microbial activity has other impacts on arsenic.

The presence of methylated forms of arsenic in the water column is thought to be due to the excretion of these species from algae, methylation by bacteria or the degradation of excreted or more complex arsenicals (Anderson and Bruland, 1991). MMAA and DMAA can be demethylated to arsenate by certain bacteria. The methylation or demethylation of arsenic can have an impact on the mobility. The affinity for adsorption onto organic sediments is as follows: arsenate > MMAA > arsenite > DMAA. Degradation will reduce the mobility, while it will be increased with methylation. (Mok and Wai, 1994).

7. Other Factors

Other characteristics of the sediments can have an effect on the mobilization of arsenic. Sediments with smaller grain sizes have been found to contain significantly higher concentrations of trace metals. Sediments with higher clay content will be more effective in the adsorption and immobilization of trace elements because of the high surface area of clay particles and due to their positive charged surfaces, which attracts the dissolved arsenic. The larger area to mass ratios of smaller particles allows for an increased coating of iron and manganese oxides, which act as scavengers and increase the arsenic concentration (Mok and Wai, 1994).

In organic matter, humic acids (the degradation-resistant portion of organic matter) have the strongest affinity for adsorption of arsenic. In acidic environments, the retention of arsenic by humic acids may be more important than clays and metal oxides (Mok and Wai, 1994).

Under laboratory conditions, the effect of temperature on the retention of arsenic by stream muds and sediments has been studied. The result was that at temperatures from 4-10 °C, the distribution coefficients were determined to be 40% less than at 20-25 °C. Therefore, a decrease in mobilization of arsenic is predicted for periods of low water temperature (Mok and Wai, 1994).

F. Summary of Relevant Guidelines

1. Sediments and Soils

The Northwest Territories do not have their own set of guidelines for contaminants in sediments and soil. The guidelines set by Environment Canada, the Ontario Ministry of the Environment and Energy (MOEE), and the Canadian Council of Ministers of the Environment (CCME) were used in this study to help interpret whether the concentrations of contaminants are a potential risk to the environment.

Guidelines are defined to be numerical limits or narrative statements recommended to support and maintain uses of the environment (CCME, 1997). They allow for a preliminary determination of whether or not a site contains contaminants at concentrations with possible adverse biological effects. They are to be evaluated in conjunction with the local background concentrations and site-specific biological assessments (Environment Canada, 1995). These guidelines are not legal requirements for reclamation at sites with contaminant levels exceeding the set criteria.

The current guidelines use total arsenic concentrations for the recommended allowable concentrations. This simplifies the required analysis of samples for comparison with criteria. These levels provide a basis point for the determination of the danger posed by arsenic at a given concentration. The speciation of arsenic, in conjunction with the local background concentrations and site-specific biological assessments, is required to develop a comprehensive risk assessment of a contaminated site.

The analysis of sediment samples in this study includes a number of elements other than arsenic to help determine the sources of contaminants in the study area. The guidelines for these elements are included, if they exist, to provide a basis for the comparison of the determined concentrations with the set criteria.

The Interim Sediment Quality Guidelines (Table II-3) from Environment Canada (1995) were created to allow for the evaluation of sediment quality prior to the development of national sediment quality guidelines by the CCME. They are based on the available toxicological information. Two assessment values are set and represent the total concentration of an element in the surficial sediments base on dry weight. The threshold effect level (TEL) is the concentration below which adverse effects rarely occur. The probable effect level (PEL) is the concentration above which adverse effects are predicted to frequently occur.

The Ontario Sediment Quality Guidelines were created to help determine the degree of contamination of sediments and what levels are severe enough to consider the removal or covering of contaminated sediments. Two assessment values similar to those set by Environment Canada are used. The Lowest Effect Level (LEL) is the level at which no negative effects on the majority of the benthic organisms is expected. Sediments surpassing the Severe Effect Level (SEL) are considered heavily polluted and will likely affect the health of benthic organisms. A management plan to remove the sediments and/or control the source of contaminants may be required (Persaud *et al.*, 1992).

Table II-3: Sediment quality guidelines for metals set by Environment Canada (1995) and the MOEE (1996).

	Environment Canada		**MOEE**	
METAL	**Threshold Effect Level (ppm)**	**Probable Effect Level (ppm)**	**Lowest Effect Level (ppm)**	**Severe Effect Level (ppm)**
Arsenic	5.90	17.0	6	33 *
Cobalt			50	
Copper	35.7	197	16	110 *
Iron (%)			2 *	4 *
Manganese			460 *	1100 *
Nickel	18.0	35.9	16	75 *
Zinc	123	315	120	820 *

*Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario (Persaud *et al.*, 1992).

The CCME Recommended Canadian Soil Guidelines (Table II-4) is meant for general guidance, and is not legally binding. The recommended arsenic concentrations are measures of total inorganic arsenic (CCME, 1997).

Table II-4: CCME Recommended Canadian Soil Quality Guidelines (CCME, 1997)

Metal	Agricultural	Residential/ Parkland	Commercial	Industrial
Antimony*	13	13	40	40
Arsenic	12	12	12	12
Copper	63	63	100	100
Zinc	200	200	380	380

*No sediment quality guidelines are given for antimony by Environment Canada or the MOEE. However, surface soil remediation criteria are given for three land uses (same as CCME) in a potable groundwater situation in the Guideline for use at Contaminated Sites in Ontario (MOEE, 1997).

2. Drinking Water

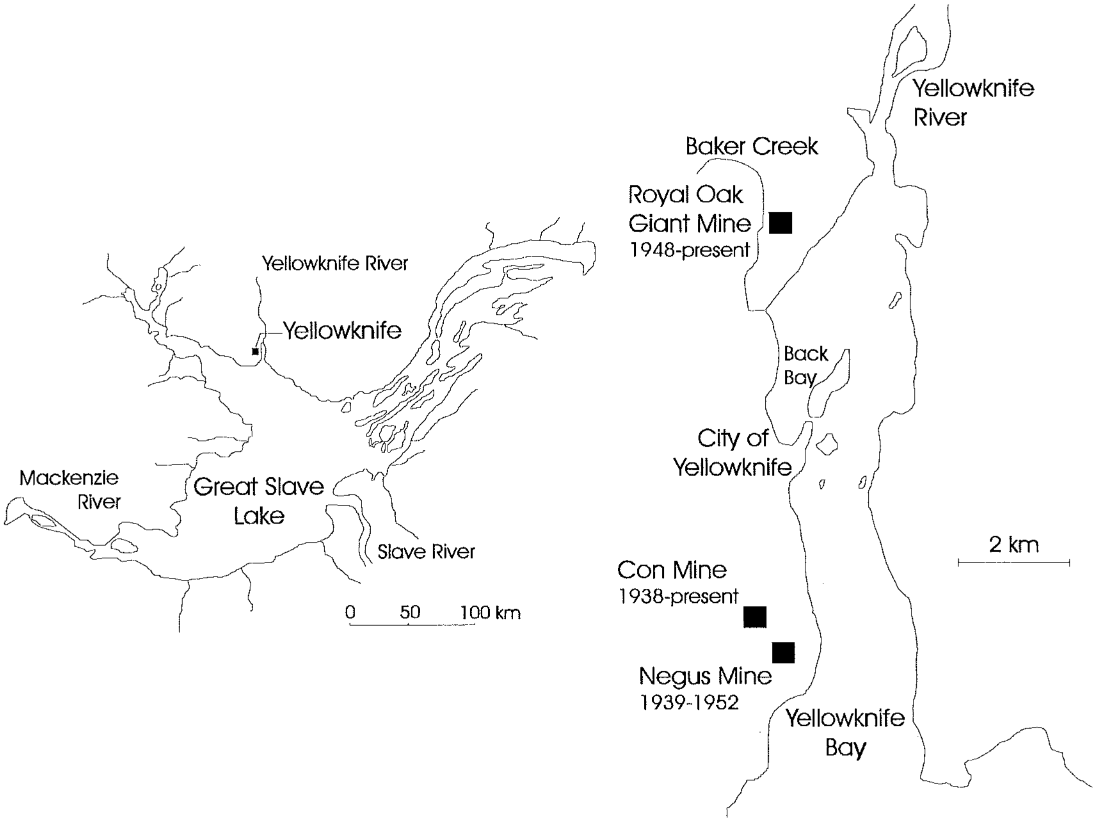
The Canadian Water Quality Guidelines have set the recommended maximum level of arsenic to be 50 ppb for drinking water and for freshwater aquatic life (CCREM, 1995). However, Health Canada and the MOEE have set the Interim Maximum Allowable Concentration (IMAC) at 25 ppb (Health Canada, 1996; MOEE, 1994). The concentrations set by the MOEE are concentration objectives above which known or suspected adverse effects occur. There is presently insufficient toxicological information on arsenic to set a Maximum Allowable Concentration (MAC) (MOEE, 1994).

The United States Environmental Protection Agency (USEPA) has set their Maximum Contaminant Level (MCL) for arsenic in drinking water at 50 ppb. It is currently under review with the possibility of it being lowered even further to 2 ppb (Reid, 1994). The USEPA is required by the Safe Drinking Water Act Amendments of 1996 to provide a final ruling on allowable levels of arsenic in drinking water no later January 1, 2001 (USEPA, 1998). The regulation is to be based on the quantified link between skin cancer and arsenic with the hazard of internal cancer being taken into account. The USEPA has mapped the concentration of arsenic in the water systems of the United States. Groundwater systems, especially those to the west of the Mississippi River, were found to have the highest incidence of elevated arsenic concentrations (Reid, 1994). The cost for compliance with the reduction of the MCL for arsenic to 2-20 ppb is estimated at $74 million annually for 20 ppb and $2.1 billion annually for 2 ppb (Pontius, 1994).

III. GIANT MINE

A. Location

The City of Yellowknife is situated on the western shore of Yellowknife Bay, which measures approximately 11.3 km long and 2.8 km wide. To the north, Yellowknife River empties into the Bay, which is on the northern shore of Great Slave Lake. The Royal Oak Giant Mine (Photo III-1) is situated approximately 5 km north of Yellowknife (Map III-1) on land leased from the Canadian government (Mudroch *et al.*, 1989).



Map III-1: Location of Yellowknife on Great Slave Lake and the Yellowknife Area.

Two other mines are situated to the south of the City of Yellowknife: 1) the Negus Mine milled up to 200 tonnes of ore per day between 1939 and 1952, 2) the Con Mine currently operates at 640 tonnes of ore per day and has been in operation since 1938 (Sutherland, 1989).

Photo III-1: Royal Oak Giant Mine

The Giant Mine has played an important part in Yellowknife's economy since it began mining gold in 1948. In recent years, the mine has undergone three changes in ownership. In 1986, Giant Resources of Australia bought the Giant Mine from Falconbridge Nickel Mines Ltd. In 1990, controlling interests were sold to Royal Oak Resources Ltd. Royal Oak Mines Inc. was formed in July of 1991 with the amalgamation of Royal Oak Resources Ltd., Giant Yellowknife Mines Ltd., Pamour Inc., Pamorex Minerals Inc. and Akaitcho Yellowknife Gold Mines Limited.

B. Gold recovery processes

The gold recovery process has changed over the years as new methods became available. The gold mined by Giant is contained within the mineral matrix of arsenopyrite and is termed refractory gold. The arsenopyrite must be broken down and oxidized in order to recover the gold. The mining of ore is currently done underground in one of three shafts as open pit operations ceased in 1990. A simplified flowsheet for the mill is given in Figure III-1.

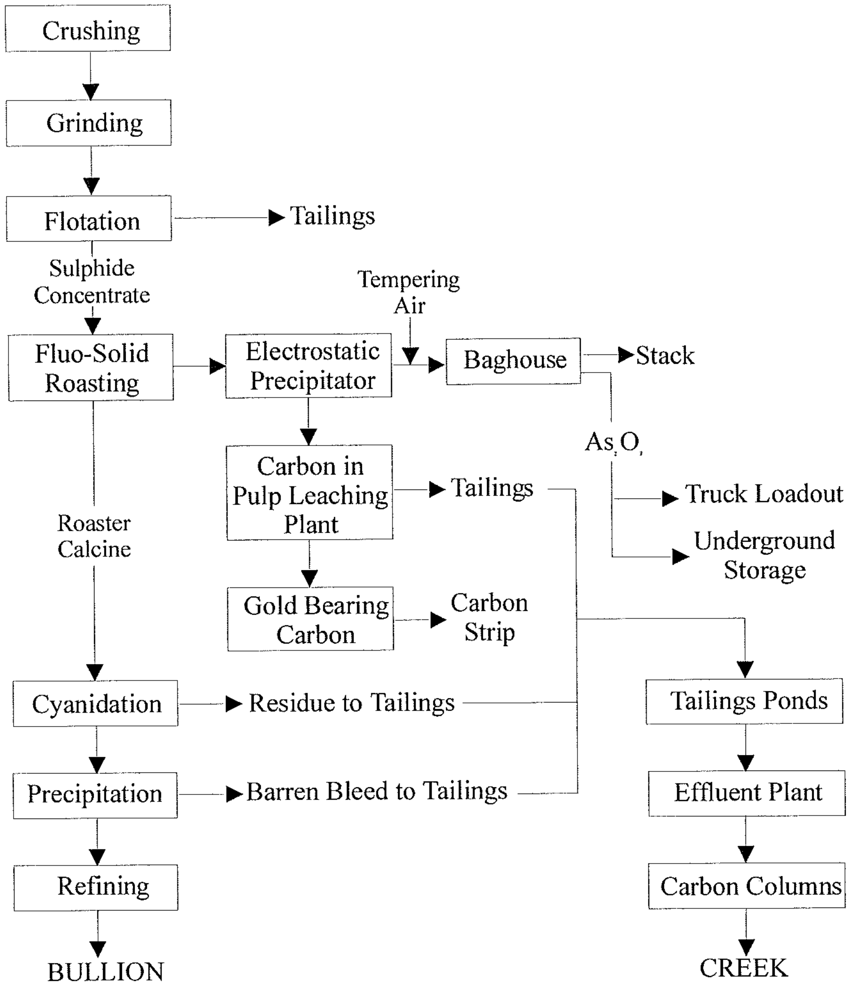


Figure III-1: Giant Mine – Simplified Mill Flowsheet (Halverson and Raponi, 1987)

1. *Crushing and Grinding*

Ore is first blasted and then removed from the shaft and brought to the crusher where it is reduced to less than 3/8th of an inch. The crushed ore is stored while waiting further grinding. The ore is then mixed with water and enters a ball mill. Working in conjunction with spiral classifiers, the larger particles are separated for further grinding and the fine particles are passed onto the next stage.

2. *Flotation*

A flotation technique is used to recover 95% of the gold in a sulphide rich concentrate. The sulphide minerals within the ore are primarily pyrite and arsenopyrite. Within the ball mills, copper sulphate is added to coat the sulphides within the ore. These treated sulphides then have an affinity for the chemical xanthate. When air is bubbled through the mixture, the xanthate coated sulfides rise to the surface where they are skimmed off and dewatered. This step acts primarily as a mass reduction step. Approximately 1300 tonnes of ore are processed each day. After the flotation stage, 1100 tonnes are deposited directly into the tailings ponds. The remaining 200 tonnes are thickened to 75% solid prior to further treatment in a two stage fluid bed roaster.

3. *Roasting*

The roaster breaks down the structure of the arsenopyrite in order to make the gold accessible. The sulphur and arsenic contained within the pyrite and arsenopyrite are oxidized by the addition of air within the roasters. This process produces gaseous arsenic trioxide and sulphur dioxide, which constitutes the majority of arsenic and sulphur within the ore. The remaining ore is called calcine and is primarily composed of the iron oxides. These iron oxides are broken down and the gold is exposed by passing the calcine through another grinding process.

4. *Cyanidation*

Sodium cyanide is added to the alkaline calcine solution, which produces a gold cyanide complex with the gold in dissolved form. The leaching process is repeated with the residual calcine being disposed of in the tailings ponds. The dissolved gold and cyanide is precipitated onto zinc dust which is then filtered out of the solution and melted to form the bullion (Royal Oak, 1997). Prior to 1976, the gold extraction was achieved using mercury amalgamation and cyanidation (Mudroch *et al.*, 1989).

5. *Gold Recovery and Future Reserves*

The mine recovers approximately 8 g of gold/ton of ore with the ability to mine 1300 tonnes of ore per day. Over the last five years, the mine has produced roughly 93 000 ounces of gold annually. In order to determine the life of the mine, three main factors were taken into account by the mine.

It was assumed that the price of gold would increase from the low value in the fall of 1997 of US$320 per ounce. This is an important factor since the cost of producing an ounce of gold, taking into account depreciation and amortization, is estimated at US$374 (Royal Oak, 1997).

The current reserves of mineable ore are estimated at 553 269 ounces of gold, which include the reserve of 140 000 ounces at the nearby Nicholas Lake deposit. This amount allows the Giant Mine to operate until the end of 2004. However, the total amount of gold at the Giant Mine site is estimated to be 2 000 000 ounces. It is assumed that at least a portion of this will become mineable once exploration is complete (Royal Oak, 1997).

In 2006, the Northwest Territories Environmental Protection Act will take full effect. Under this act, the mine would have to reduce its sulphur dioxide emissions by 90%. The current position of the mine is that it cannot justify the expenditure of $35 to $42 million (Environment Canada, 1997) to meet the standards without the discovery of a significant new gold deposit (Royal Oak, 1997).

C. Aerial emissions

The Giant Mine's aerial emissions consist primarily of arsenic trioxide and sulphur dioxide. As noted above, these off-gases are created during the roasting stage. Over the years, the amounts of sulphur dioxide and arsenic trioxide that were released decreased due to the development and addition of emission control devices. Table III-1 illustrates the reduction in arsenic trioxide emission rates over the years.

Currently, the off-gases from the roaster are passed through an electrostatic precipitator, which removes the fine particulate matter for further gold extraction. The gas is cooled and passed through a baghouse. The cooling causes the arsenic trioxide to condense and allows it to be collected in dust collectors. The gas, composed primarily of sulphur dioxide and air, is then emitted through a 150 ft stack (Royal Oak, 1997).

Table III-1: Arsenic emissions from the Giant Mine (Environment Canada, 1997)

YEAR	ARSENIC (kg/day)
1950	7300
1955	2900
1960	75
1966	240
1970	220
1975	76
1981	17
1985	24
1990	37
1995	3.2

Even with the reductions in arsenic emissions over the years, it is estimated that a total of 20 700 tons of arsenic have been emitted into the environment by the Giant Mine since 1948 (Environment Canada, 1997). These emissions have had an effect on arsenic levels in the soils of Yellowknife with levels ranging from 500 to 1500 ppm, depending on the location (Hutchinson *et al.*, 1981).

Although the arsenic emissions have been reduced greatly, there is still great public concern regarding the fate of the arsenic trioxide removed in the baghouse. Arsenic trioxide is currently being stored in underground vaults within the mine shafts. Once full, these shafts are capped with a cement wall. At present, there are approximately 270 000 tonnes of baghouse dust containing ≈200 000 tonnes of arsenic trioxide within the vaults with 15 tonnes of dust being added daily (Royal Oak, 1997). The mine shafts are located below the groundwater table, which raises the concern that groundwater contamination will occur because arsenic trioxide is both relatively toxic and soluble. At present, a complete study of the groundwater table and its flow has not been conducted.

An air dispersion model for current roaster stack emissions of arsenic and sulphur dioxide for the Giant Mine has been completed (Dillon, 1995). The model showed that the Ontario Guideline of 0.300 $\mu g/m^3$ for arsenic in ambient air would not be exceeded in the populated areas in the region of the mine (Environment Canada, 1997).

D. Tailings

The mine tailings are produced in the electrostatic precipitator, the flotation and the cyanidation stages. Groundwater is continuously pumped from the mine and is added to the tailings ponds for further treatment (Halverson and Raponi, 1987). The containment and treatment of effluent from the ponds has changed over the years (Photo III-2).

At the beginning of mining operations, tailings were discharged directly into Baker Creek and the area referred to as the Beach Tailings Area to the east of the mine on the shore of Yellowknife Bay. The marked extent of the Beach Tailings is an estimation of the area covered by direct deposition of tailings based on information obtained from historical data, air photographs (Photo VI-1 and Photo VI-2), sediment samples and visual inspection of the site. The Beach Tailings Area continued to be used until the construction of the Central Pond in the mid-1950's. The North, South and Northwest Ponds were constructed as needed in the 1960's, 1970's and 1987, respectively (Photo III-2, Photo III-3 and Photo III-4) (Schultz, 1998).

For the design and construction of the tailings ponds, natural depressions were used as much as possible to reduce the required number of dams. Where dams were necessary, they were made with compacted clay cores with rock-fill exteriors. The clay was of low permeability so as to reduce the amount of seepage. Rock-fill was used to reduce the erosion of the clay. Of the four ponds, only the South Pond is no longer used. The Northwest Pond receives the produced tailings except for when there are problems with the piping system. When this occurs, the Central and North Ponds receive the tailings. The Northwest Pond will remain the main pond for the next several years, with the current plan of raising the dams on the North Pond in order for it to be operational for another three years (Royal Oak, 1997).

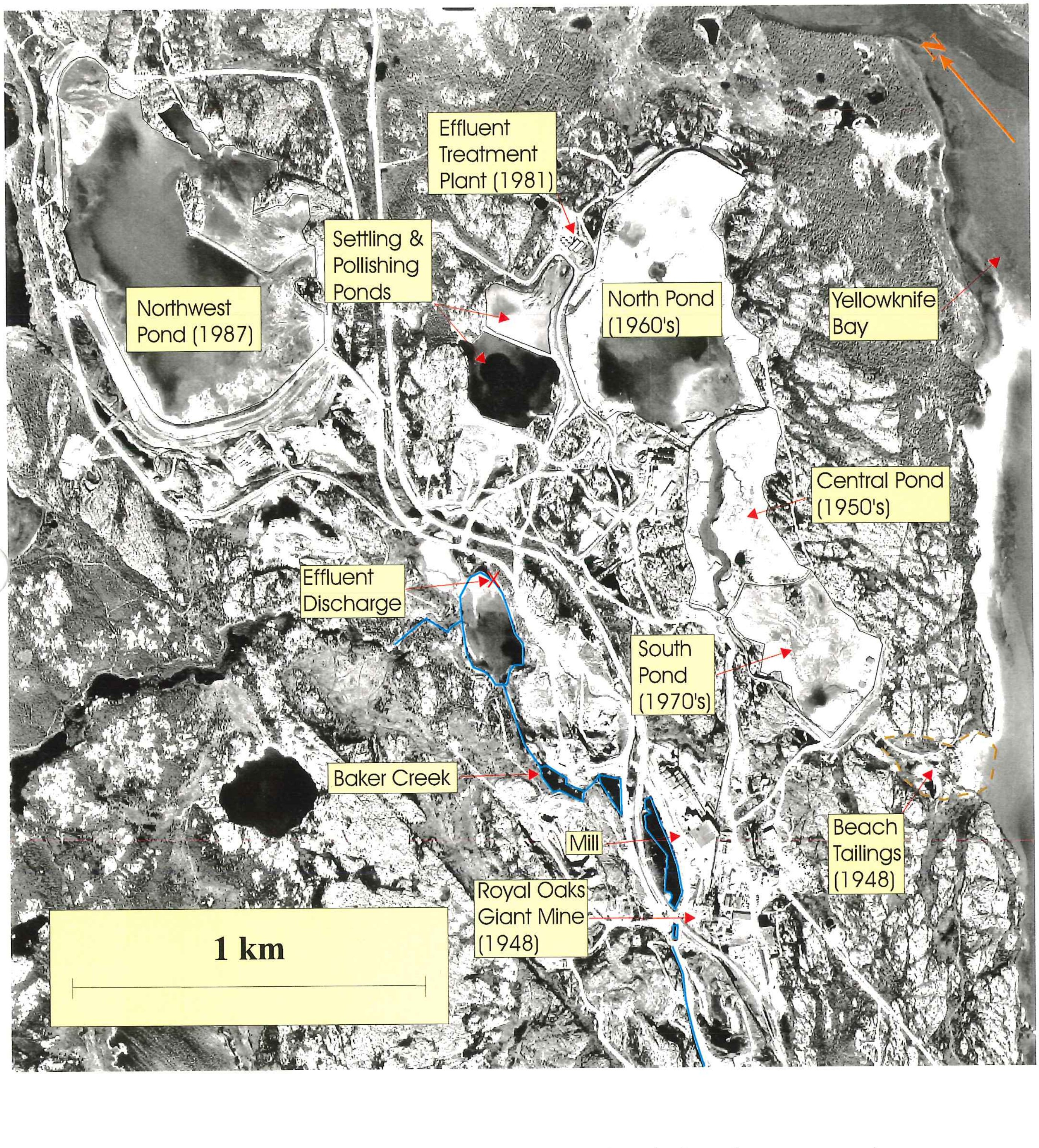


Photo III-2: Royal Oak Giant Mine site location

Photo III-3: Northwest Tailings Pond facing North

Photo III-4: View of the South Pond with Yellowknife in the distance. Taken from the Central Pond.

E. Effluent Treatment

The Giant Mine operates under a water use license, which regulates the amount of water that can be used as well as the quality of the effluent discharged into Baker Creek. The maximum annual water consumption set by the license is 1 950 000 m^3. Between 1993 and 1996, water consumption did not surpass 1 700 000 m^3. The current license expires April 20, 1998. Water board hearings have been held over the winter concerning the mine's request for an additional term ending April 30, 2008.

The tailings slurry, which consists of 94% water by volume and 15% solid by weight, is deposited into the tailings ponds. The effluent accumulates during the seven winter months and is then treated during the summer season.

Prior to 1981, cyanide removal was left to natural degradation. Arsenic removal employed a two-step method, which raised the effluent pH to 12.0 at which point the arsenic precipitated out. Concern arose with respect to insufficient degradation of cyanide, as well as the fact that the pH decreased to 8.5 which led to partial dissolving of the arsenic (Halverson and Raponi, 1987).

These concerns led to research conducted in 1976 by the Giant Mine and Environment Canada with the aim of improving the quality of the effluent discharge from the mine. The result of their efforts was, in 1981, the first alkaline chlorination and ferric sulphate effluent treatment plant at a gold mine in North America. The process was modified from alkaline chlorination to hydrogen peroxide oxidation in 1990 to eliminate the problems arising from the residual chlorine. A diagram outlining the current method for treatment of waste water can be seen in Figure III-2.

All effluent streams are deposited into the tailings ponds throughout the year where settling occurs due to gravity. During the summer months, the clear surface water is decanted to the effluent treatment plant. In order to treat cyanide, copper sulphate is added as a catalyst for the oxidation of the cyanide compounds. Hydrogen peroxide is added and pH is controlled at 9.2 by the addition of lime. The cyanide is oxidized to form cyanate which then breaks down to carbon dioxide and nitrogen.

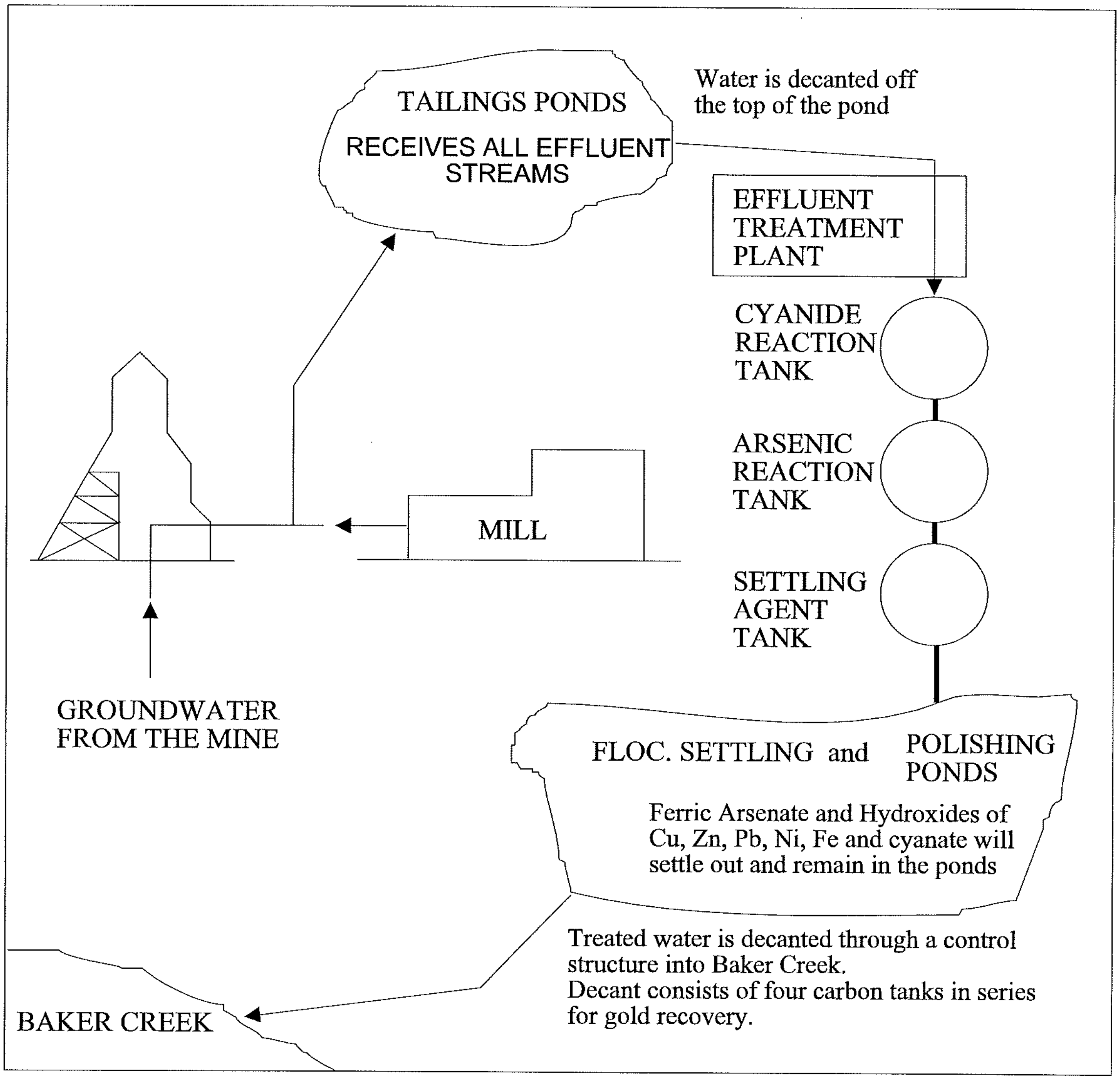


Figure III-2: Treatment of waste water at the Royal Oak Giant Mine [adapted from (Halverson and Raponi, 1987)]

In the arsenic reaction tank, ferric sulphate is added to reduce the pH to 7.0, resulting in the reaction shown by the following equation.

(7) $Fe_2(SO_4)_3 + 12(H_2O) \rightarrow 2Fe(OH)_3{\bullet}6H_2O + 3SO_4^{-2} + 6H^+$

These conditions cause the arsenic to precipitate as ferric arsenate. The pH is then raised to 8.5 with the addition of lime so that other metals precipitate out as insoluble hydroxide compounds. These precipitates are allowed to settle in the settling tank and the secondary polishing pond. Carbon adsorption columns are used as the final step to recover gold and various cyanide complexes of other metals. The water is then discharged into Baker Creek at the location indicated in Photo III-2 (Royal Oak, 1997).

There is some doubt as to the actual form of arsenic within the tailings ponds. As opposed to precipitating out as ferric arsenate, it is possible that the arsenic may simply be co-precipitating out with the ferric hydroxide (Cullen, 1998). The arsenic could be present in a number of other phases including scorodite ($FeAsO_4 \bullet 2H_2O$) (Azcue and Nriagu, 1994), various Ca-Fe arsenate hydrates, iron hydroxides and secondary sulphides.

This effluent treatment process has proven to be successful. Final effluent discharge levels in 1981 were as follows: arsenic – 7.52 ppm, cyanide – 11.65 ppm and copper – 6.85 ppm. In 1986, the levels and the percent decrease were 0.18 ppm (97.6%), 0.74 ppm (93.6%) and 0.33 ppm (95.1%), respectively (Halverson and Raponi 1987). The current water license outlines maximum allowable concentrations of contaminants in the effluent discharge (Table III-2).

Table III-2: Allowable contaminant levels in discharge

Parameter	Maximum Average Concentration (mg/L)	Maximum Concentration of any Grab Sample (mg/L)
Total Cyanide	0.80	1.60
Total Arsenic	0.50	1.00
Total Copper	0.30	0.60
Total Lead	0.20	0.40
Total Nickel	0.50	1.00
Total Zinc	0.20	0.40
Suspended Solids	15.00	30.00
Total Ammonia	19.50	
Oil and Grease		5.00
pH	Between 6.0 and 9.5	

The maximum average concentrations have not been exceeded between 1993 and 1996. The allowable arsenic concentration was lowered from 0.80 mg/L to the current 0.50 mg/L as of January 1, 1994 in order to meet the guidelines set by the federal Metal Mining Liquid Effluent Regulations. The average annual release of arsenic by water has been 1412 kg, 609 kg, 450 kg and 515 kg during this four year period (Royal Oak, 1997).

F. Reclamation Outline

The current water license requires that the Giant Mine develop a more comprehensive reclamation plan for the mine site than the one presently in place. This plan has been incorporated into the current Abandonment & Restoration Plan for final closure found in the Water Licence Application (Royal Oaks, 1997). This is of great importance to the people of Yellowknife as some forecasts predict that the mine will close within eight years.

1. Surface Contamination and Infrastructure

The proposed plan consists of the dismantling of all structures and buildings. All equipment of any value will be sold with the remaining non-hazardous equipment to be left underground or placed in an open pit. All hazardous equipment and materials will be removed from the site for proper disposal. All of the openings into the mine will be closed with concrete caps.

The only surface contaminant found by Royal Oak Mines to exceed the CCME guidelines was arsenic at levels far exceeding the 50 ppm level. Royal Oak believes that a large portion of this arsenic is from natural sources. Leachate tests were conducted by the mine to determine the availability of the arsenic. Eight specific areas, generally in close proximity to the roaster and baghouse plants, were shown to have higher levels of more soluble forms of arsenic. These soils are to be removed and placed in the tailings ponds where any leachable arsenic will be treated by the effluent treatment plant. Royal Oak proposes to develop a site-specific criterion for arsenic, which may differ from the current criteria (Royal Oak, 1997). These plans were based on the old CCME criteria for arsenic at commercial sites of 50 ppm. The criteria for arsenic has since been reduced to 12 ppm for industrial sites (CCME, 1997).

Several areas on the mine site have been contaminated with hydrocarbons contaminants due to fuel handling and transfer facilities. Landfarming is proposed to remove this contamination (Royal Oak, 1997).

2. Arsenic Trioxide

A cleanup solution for the arsenic trioxide from the baghouse dust has not yet been determined. This issue will addressed in the new water use license. Various options are currently being studied and will be addressed in the new water use license. They include:

- Re-establishment of the permafrost into the storage chambers to immobilize the arsenic trioxide.
- Diverting the groundwater around the storage chambers.
- Removal of the arsenic trioxide from the storage chambers followed by:
  - Disposal of the dust in a suitable storage facility
  - Conversion of the arsenic trioxide to the more stable ferric arsenate for subsequent disposal
  - Conversion of the arsenic trioxide to a higher purity for subsequent sale.

3. *Mine Tailings and Effluent Treatment*

A major concern with respect to many mine tailings is their potential for the creation of acid rock drainage (ARD). Royal Oak believes that the tailings are not a source of ARD because they have found that the tailings can neutralize between 10 to 15 times as much acid as they can generate. It is therefore believed that any ARD that is produced will be neutralized by the carbonate materials found within the tailings.

The mine investigated the feasibility of reintroducing permafrost into the tailings in order to reduce problems with leachate. A number of sections were covered with various depths of mine wastes, as well as a high density polyethylene liner. These areas are visible in the aerial photograph of the mine (Photo III-2) at the bottom right of the South Pond.

The introduction of a permafrost layer was not found to be possible (Royal Oak, 1997). However, it was noted that the layers did act as thermal barriers and kept the tailings frozen during the spring runoff. This is the period of greatest water transport and hence poses the greatest risk. At each of the test cells, groundwater monitoring wells were installed. Throughout the monitoring period, little movement of groundwater was found. This could indicate that contaminated leachate does not pose a threat to the groundwater in the tailings areas.

It is, however, important to establish the long-term stability of the tailings themselves. The purpose of any chosen capping technique would be to immobilize the contaminants within the tailings and to allow for the development of vegetation. The plants would help reduce both wind and water erosion. One possible substance to use as a future cover is the mill flotation tailings, which have proven to be capable of supporting plant growth. These tailings are low in soluble contaminants and process reagents (Royal Oak, 1997).

Regardless of the chosen reclamation plan, the Effluent Treatment Plant is to continue operating as long as there is contaminated water to be treated. This includes water from the tailings ponds or water pumped from the mines (Royal Oak, 1997).

G. Previous Studies

A number of studies have been conducted on the Giant Mine and in the Yellowknife Bay area. One study (Hutchinson *et al.*, 1981) examined the levels of arsenic contamination in soil surrounding the Giant Mine, the Con Mine and the City of Yellowknife. Arsenic concentrations up to 9300 ppm and 5000 ppm, at the Giant and Con Mines, respectively, were found. At the various soil sample locations, it was determined that the arsenic levels were highest in the 0-4 cm range, and dropped off rapidly at greater depths.

Mudroch *et al.* (1989) determined the sedimentation rate and the concentrations of arsenic and zinc at depth at two locations in Yellowknife Bay. The composition of the sediments indicated that anthropogenic input of contaminants occurred in the area over the past 50 years. The age profile of the contaminants were consistent with the changes in mine operations over the years.

Sutherland (1989) determined the levels of various metals within similar areas to the study by Mudroch, and their subsequent effect on the benthic community. The abundance and species numbers of benthic macroinvertebrates within Yellowknife Bay were shown to be greatly reduced. The contaminant profile was determined to reflect the changes in environmental practices at the mine.

Jackson *et al.* (1996) conducted a study on Yellowknife Bay to answer three questions: 1. Is the water safe to drink? 2. Is the water safe to swim in? and 3. Are the fish safe to eat? It was determined that the water was safe to drink and to swim in except in the area of the Baker Creek outlet into Yellowknife Bay. The concentrations of various metals observed in the tissue of various fish were elevated, but they were below any limits set for human consumption.

Environment Canada (1997) published a report on arsenic releases in the environment of the Northwest Territories. This included comprehensive information on the historical aerial emissions by the Giant Mine, and an investigation into possible technologies for the reduction of emissions at the Giant Mine. The roaster at the Giant mine is the only anthropogenic source for aerial emissions of arsenic in the Northwest Territories. The processing technologies, which would eliminate the aerial emissions, require significant capital expenditures ($35 000 000 to $42 000 000). However, alternative treatment technologies that would reduce the emissions from the present 30 kg/day to 1 kg/day are readily available at lower cost ($1 200 000 to $2 200 000).

IV. METHODS

A. Sampling Procedures

The samples for this thesis were collected during two one week periods beginning June 22, 1997 and August 23, 1997, respectively. Samples included: surface sediments, sediment cores, sediment porewater, tailings and surface water.

Surface grabs were obtained using an Eckman grab. Sediments were placed into Whirlpack^{TM} bags using sterilized plastic scoops. These samples were placed in chest freezers within 3 hrs. of sampling. At locations situated above water, the samples were simply collected with a sterilized plastic scoop and placed into Whirlpack^{TM} bags.

Sediment cores were obtained using a gravity corer deployed from a small boat. The corer consisted of a 120-cm long polyacrylic tube measuring 9-cm in diameter. The tube was attached to a modified Kajak-Brinkhurst (KB) gravity corer (Photo IV-1). The cores were collected by lowering the corer into the sediment. Within 3 hrs of taking the core, the samples were placed in a walk-in cooler kept at 4°C. All cores were processed within 14 hrs. of collection.

Photo IV-1: Modified Kajak-Brinkhurst gravity corer

Porewater samples were obtained by sectioning the cores at 5-cm intervals within a nitrogen filled glove bag. The sediments were squeezed under nitrogen through a 0.22 µm Millipore filter using established methods, Photo IV-2 (Reimer, 1989). The samples were collected under nitrogen in Evergreen^{TM} containers, which were immediately frozen using dry ice. A nitrogen atmosphere was used to ensure that the chemical forms of arsenic, manganese and iron present would be maintained.

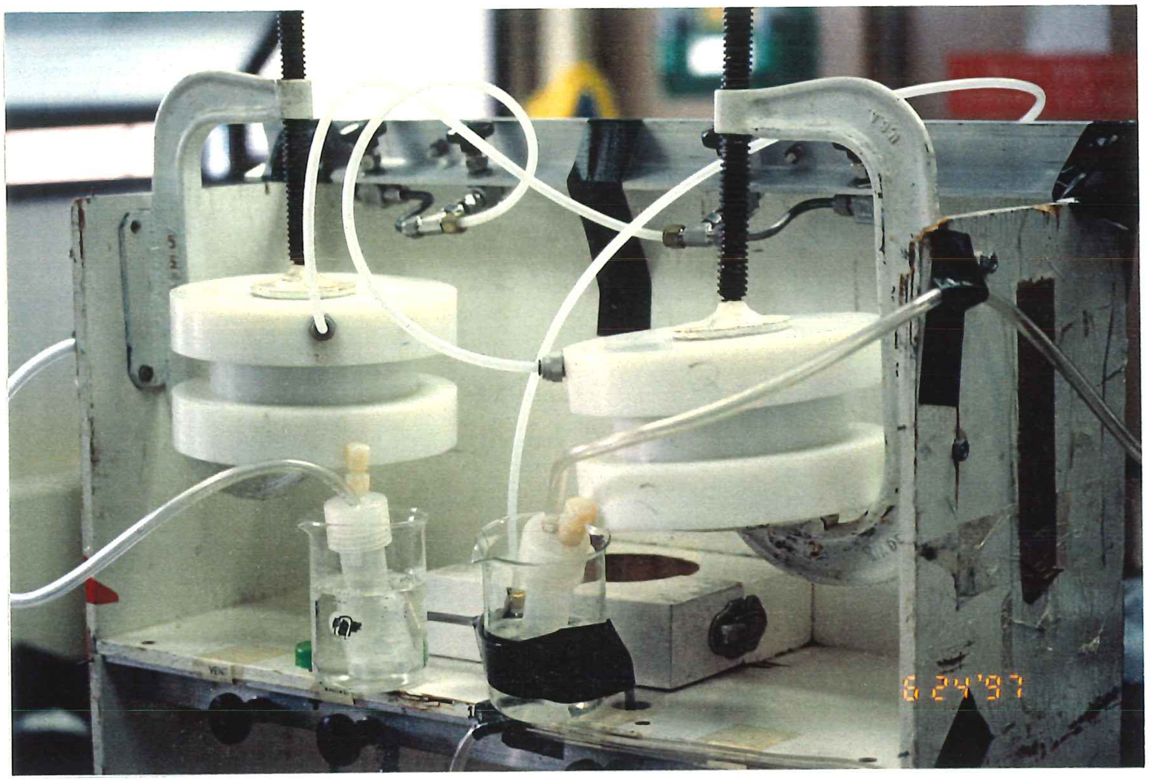


Photo IV-2: Apparatus used to obtain porewater samples.

Surface water samples were collected directly into acid washed 1-L polyethylene bottles. For shallow locations, only surface samples were obtained. At deeper locations (i.e. > 4 m), a Van Dorn sampler was used to obtain water from the top and from the bottom of the water column. At depths >4m, a sample was also obtained from the middle of the water column. All samples were subsequently frozen. Prior to analysis, all samples were passed through 0.22 μm filters in order to eliminate fine particulate matter; hence, results were indication of only dissolved arsenic.

B. Sampling Locations

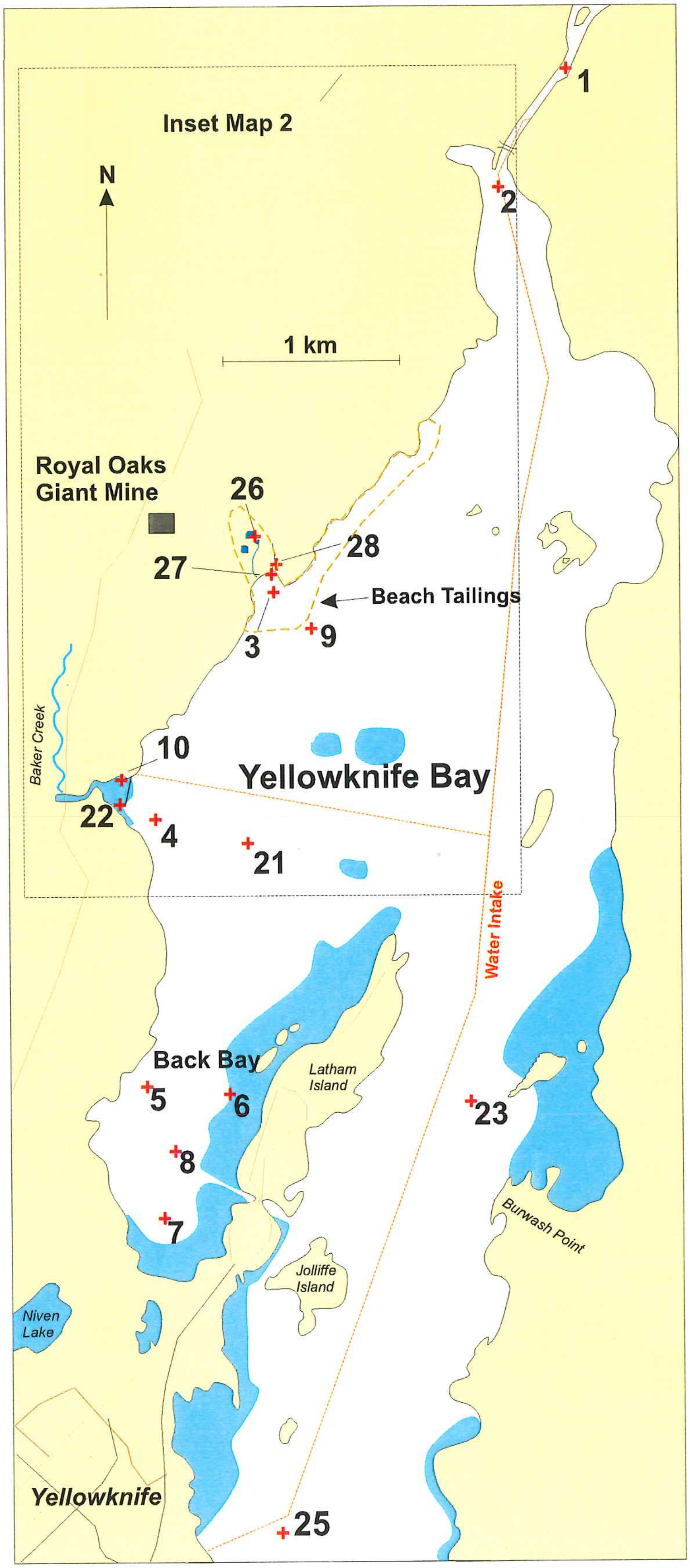
Map IV-1 and Map IV-2 show the thirty-five sampling locations in Yellowknife Bay, Baker Creek and the Giant Mine tailings ponds. Table IV-1 describes the locations of certain sample locations within Baker Creek and Yellowknife Bay.

The tailings pond samples were collected to get a general idea of the average composition of the tailings and to be able to study the stability of the arsenic throughout

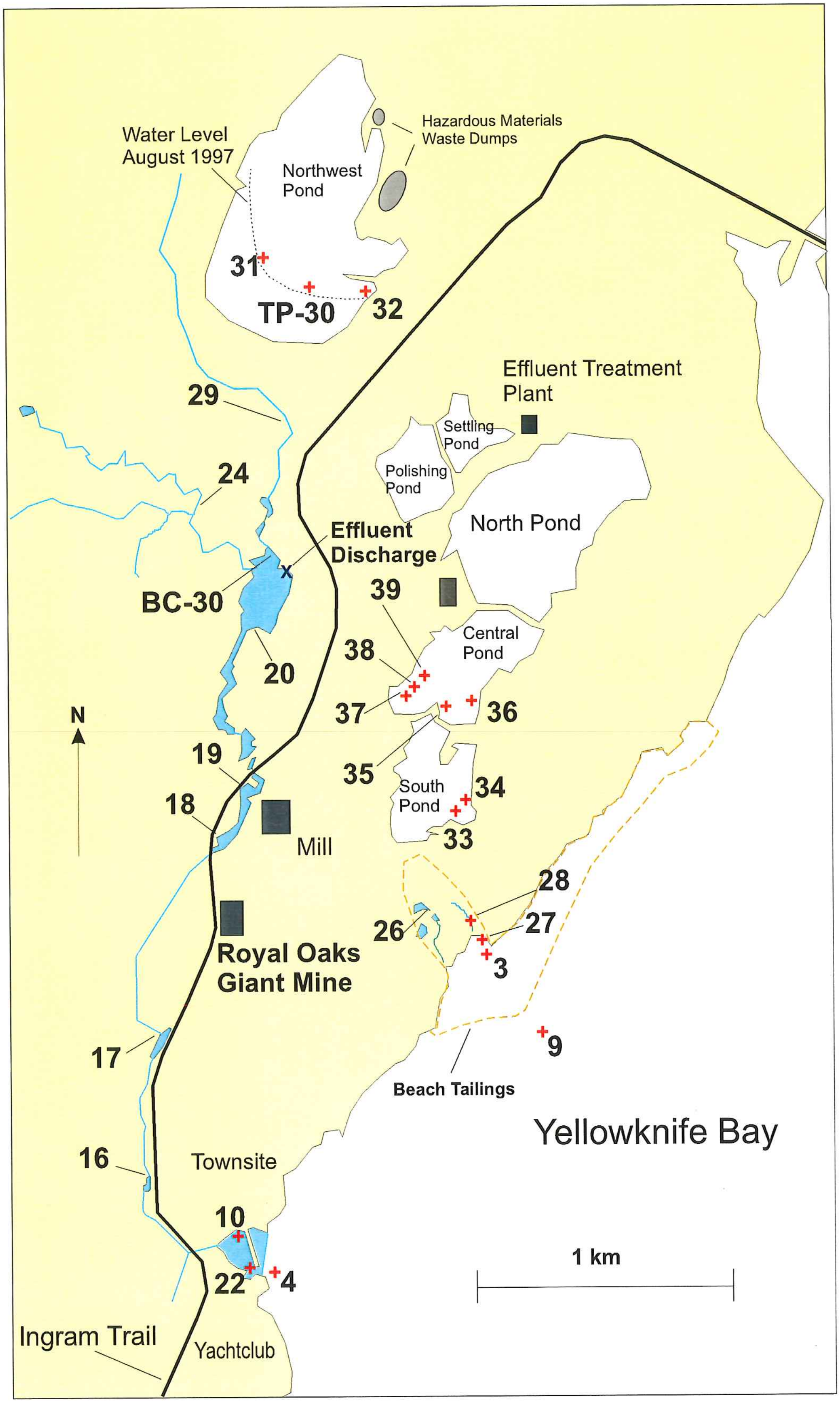
the tailings ponds. The Baker Creek samples (#10, #16 to #20, #22, #24, #29, #BC-30) covered the area affected by the effluent discharge as well as at a possible background location (upstream; #24). Sample locations #4 and #21 were chosen to map out the effect that the discharge of contaminants into Baker Creek has had on Yellowknife Bay. The sample locations near the Beach Tailings Area were selected in order to examine the characteristics of the tailings in this area and to try to determine the total area covered. The remainder of the samples in Yellowknife Bay were collected in order to get a general idea of the level of contaminants in background locations (#1) and to evaluate the extent to which the area has been influenced by aquatic redistribution of contaminants and the effects of aerial deposition (#8, #23 and #25).

Cores and/or sediment grabs were obtained at all sample locations. Water samples were collected at all locations except for those with no overlying water (#28, #BC-30, #33 to #39).

The water intake for the City of Yellowknife and the Giant Mine is indicated with the dashed red line Map IV-1. The current source of water is located near sample #1. The intake was moved to its present location from the area near sample location #25 in 1969 (Harbicht, 1998) due to concern of high levels of arsenic (Mudroch *et al.*, 1989).



Map IV-1: Sample locations from Yellowknife Bay



Map IV-2: Sample locations from the Royal Oak Giant Mine tailings ponds and Baker Creek.

Table IV-1: Description of sample locations

Sample Sites	
Mine Tailings	
#30 - #32	- three locations in the Northwest Tailings Pond - 2 m into the portion of the pond covered by water at the time of sampling
#33 & #34	- two dry locations at the southeastern edge of the South Tailings Pond
#35 - #39	- five dry locations throughout the Central Tailings Pond
Baker Creek	
24	- 500 m upstream to the northwest of the pond, which receives the effluent discharge - at a bend in the creek measuring 1.5 m across.
29	- the gravel bed of Trapper Creek running along the western side of the Northwest Pond - Trapper Creek has a smaller flow than Baker Creek and joins Baker Creek at the pond
BC-30	- the large deposit of sediments at the northern tip of the pond - In August, these sediments were above the water level
20	- mouth of the pond, 5 m from the shore (Photo IV-3)
19 & 18	- from the western shore of the widening of the creek near the mine site (Photo IV-4)
17	- 2 m from the shore in the center of a widening of the creek (Photo IV-5)
16	- where the creek widens
10	- northern edge of the Baker Creek marsh where the creek empties into Yellowknife Bay (Photo IV-6) - Sample location is covered by *Equisetum fluviatile* (horsetail) and is located 15 m from the main channel
22	- A channel 10 m wide runs unimpeded through the vegetation of the marsh and empties into Yellowknife Bay - Sample obtained from the center of the channel, 10 m from the end of the creek (Photo IV-6)

Table IV-1 (cont'd): Description of sample locations

Sample Sites	
Yellowknife River and Yellowknife Bay	
1	• center of Yellowknife River near the City of Yellowknife's freshwater intake • characterized by very hard clay sediment
9	• 500 m offshore of the Beach Tailings Area
4	• 50 m directly outside of the Baker Creek outlet
21	• 800 m directly outside of the Baker Creek outlet
8	• center of Back Bay, which is commonly used for swimming and other water activities.
23	• center of the channel between Latham Island and the eastern shore.
25	• offshore in Yellowknife Bay near the secondary freshwater intake.
Beach Area	
3	• 50 m from shore in small bay of the Beach Area
26	• collected from the northwestern pond of a grouping of three ponds found within the Beach Tailings Area
27	• 10 m from shore in small bay of the Beach Area
28	• 10 m onshore from the bed of a small, dried, water runoff area

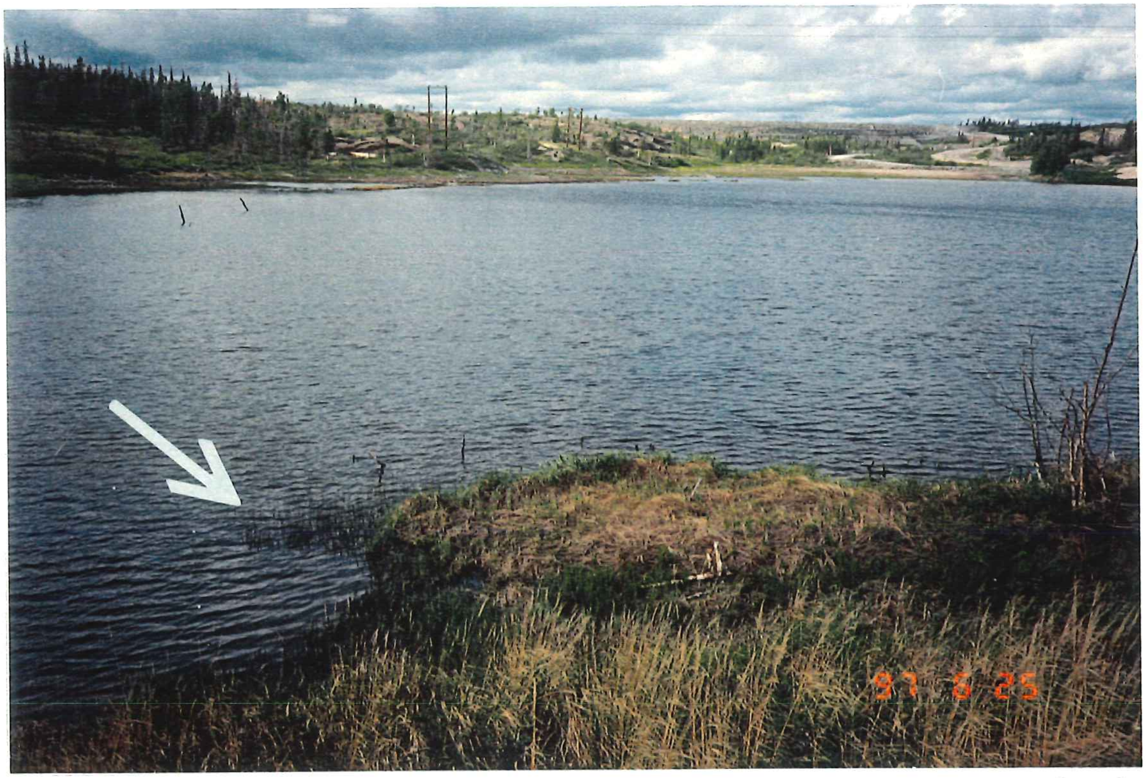


Photo IV-3: Baker Creek Lake showing location of sample #20. A dam for the Northwest Pond is seen in the background.

Photo IV-4: Baker Creek beside the mill, showing location of sample #18.

Photo IV-5: Location of sample #17 collected in August, 1997.

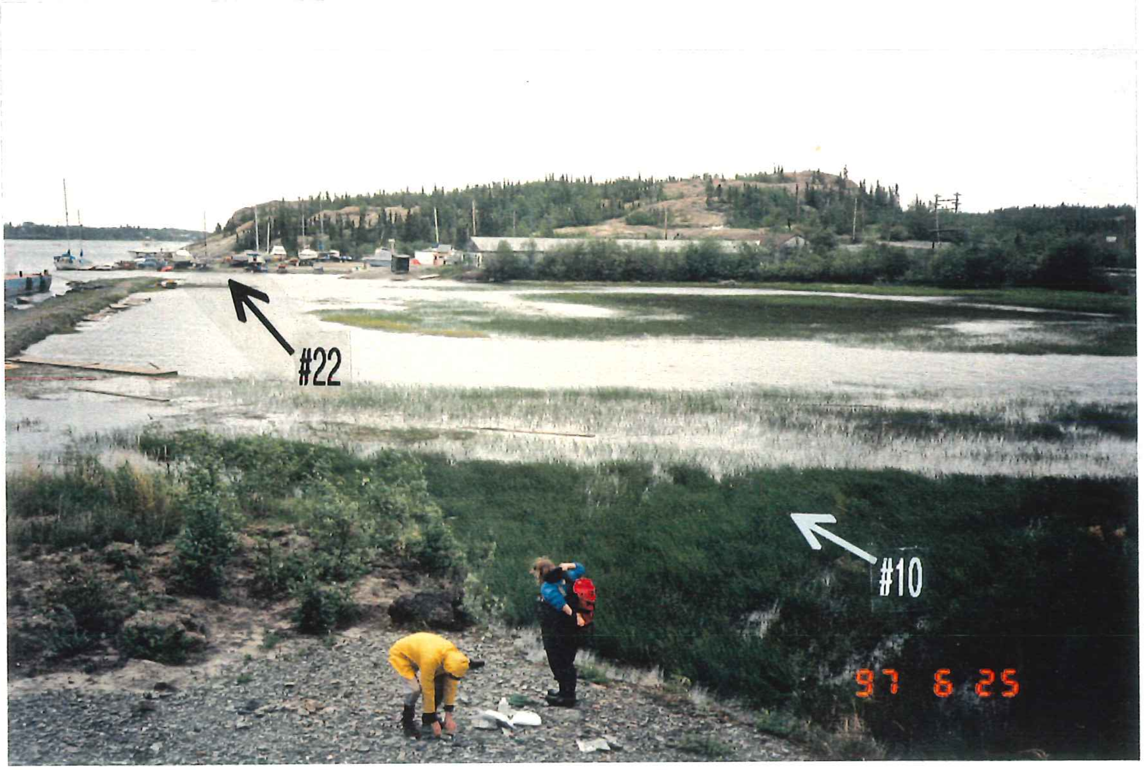


Photo IV-6: Baker Creek marsh area with location of samples #10 and #22.

C. Sample Analysis

1. Atomic Absorption Spectroscopy

Sediment and tailings samples were dried overnight and then ground to a fine powder. A small amount of sample (0.25 g), 2 mL of nitric acid and 6 mL of hydrochloric acid were combined in 50 mL test tubes. The test tubes were placed in an aluminum block, which was heated on a hot plate overnight ≈50°C until there was approximately 0.5 mL of liquid remaining. The samples were then diluted to 25 mL with distilled water (ESG, 1997). Aliquots of this solution were used for subsequent metal determination by atomic absorption (AA) spectroscopy. The concentrations of iron (Fe), manganese (Mn), copper (Cu), cobalt (Co) and nickel (Ni) were determined by direct flame injection (Allied, 1983).

The porewater and surface water samples were slowly thawed in an ice bath. The porewater samples were maintained under a nitrogen atmosphere as the containers were opened and the required amount of sample was taken for subsequent dilution and analysis.

Hydride generation was used for arsenic determination to increase the sensitivity/accuracy of measurement. This technique allows for the determination of the total arsenic concentration, which includes all of the hydride generating arsenic species of arsenite [As(III)], arsenate [As(V)], monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA). Other non- hydride forming species, such as arsenobetaine and arsenocholine, cannot be detected by this method (Le *et al.*, 1992); other methods are required for the analysis of biological samples containing these compounds.

The extracted samples were further diluted into acid washed 30 mL Qorpak^{TM} vials with 10% hydrochloric acid (HCl) and 1% w/v potassium iodide (KI). The KI reduced any As(V) present in the samples to As(III) since As(V) does not react with the sodium borohydride ($NaBH_4$) to form arsine. This reduction is complete in 50 min at room temperature or 4 min at 50°C (Brodie, 1977). The HCl ensures that the arsenic remains in the dissolved form. The hydride forming steps involve mixing the sample with 3% $NaBH_4$ and a 20% HCl solution to form gaseous arsenic hydride (Brodie, 1979). A quartz cell was used to increase the accuracy of measurements (Welz, 1985).

The calibration of the AA was conducted using a series of prepared standards ranging from 0 to 10 ppb for arsenic and 0 to 5 ppm for the other elements. The average relative standard deviation between samples extracted and analyzed in duplicate was found to be less than 12% for all metals other than iron, which had a value of 25%. A detailed summary of these values can be found in Table X-9 of Appendix B. The average relative standard deviation for arsenic analysis of the leachate, surface water, and porewater samples was determined to be 6.3%. The specific values can be found in Table X-15 of Appendix B. The certified reference material Mess-2 was used to monitor the accuracy of arsenic, cobalt, copper, manganese and nickel extraction and analysis. Reference material 1646 was used for iron. The comparison of the determined concentration with the certified values can be found in Table X-10 of Appendix B. The detection limit for arsenic analysis was determined to be 0.60 ppb in water. Five blank samples were prepared and analyzed, with the detection limit being set at three times the average standard deviation.

2. *Neutron Activation Analysis*

Neutron activation analysis (NAA) was completed using the Royal Military College's SLOWPOKE nuclear reactor. NAA is a non-destructive method of analysis with the capability for simultaneous analysis of up to 40 different elements (Bonin, 1997). Analysis was conducted by the NAA lab for the following metals: gold (Au), potassium (K), lanthanum (La), sodium (Na), antimony (Sb), zinc (Zn), arsenic and iron. The tailings and sediment samples were dried overnight and ground to a fine powder. Samples (1-2 g) were placed in a polyethylene cup measuring 1.5 mL, total volume, and analyzed. A flux of 5×10^{11} n cm^2 s^{-1} was used with an irradiation time of 2 h followed by count times of 3 h for zinc and 2 h for all other metals.

The detection limits for NAA analysis differ for each sample. The range of detection limits can be seen in Table X-11 of Appendix B. Seven certified reference materials were used for the calibration of the NAA. The average relative standard deviations between each run was generally less than 8% as can be seen in Table X-13 of Appendix B. Five samples were analyzed in duplicate producing an average relative standard deviation of less than 4% for all elements (Table X-12 of Appendix B).

3. X-Ray Fluorescence (XRF)

A TN Spectrace 9000 XRF was used for the analysis of arsenic, calcium (Ca), copper, iron, manganese, potassium, antimony and zinc. The measurement times used were 300, 100 and 50 seconds for the three radioactive isotope excitation sources, cadmium (Cd-109), iron (Fe-55) and americium (Am-241), respectively. The tailings and sediment samples were dried over night and ground to a fine powder. Approximately 5 g of sample was placed in a teflon cup and covered with mylar film.

The chosen sample measurement times coincide with the standard times used by ESG at RMC for analysis of copper, lead and zinc (ESG, 1997). These times were originally identified by the Analytical Services Unit (ASU) at Queen's University as those that maximize the accuracy of the TN Spectrace 9000 XRF while minimizing the time required for analysis. The method application for XRF analysis of arsenic and the corresponding analytical performance is covered in Chapter 5.

Ten samples were analyzed in triplicate by the XRF. The average relative standard deviations ranged from 2.0% for calcium to 16.2% for copper and antimony. These results are presented in Table X-14 in Appendix B.

4. Sequential Extraction

A five step sequential extraction was completed to determine the partitioning of the various forms of arsenic based on the procedure set out by Tessier *et al.* (1979). The results of this extraction procedure demonstrates both the bioavailability and the source of the arsenic contamination. The five fractions are:

i. Exchangeable: This phase is weakly bound and considered to be the most bioavailable.

ii. Bound to carbonates

iii. Bound to iron and manganese oxides: The Fe and Mn oxides are scavengers of large amounts of the metals in solution.

iv. Bound to organic matter: The trace metals attached to living organisms, detritus and coatings on mineral particles.

v. Residual: The trace metals found within the crystal structure of the primary and secondary minerals.

The appropriate extraction was completed on 1 g of dry sample in 50 mL centrifuge tubes. After each step, the tubes were centrifuged at 3000 rpm for 30 min. The supernatant was removed and analyzed. The residue was rinsed by adding 8 mL of distilled water, shaking for 15 minutes, and centrifuging for 15 min. The supernatant was analyzed for total arsenic concentration by AA using the method previously described (section IV.C.1 Atomic Absorption Spectroscopy). The five extraction steps were as follows:

i. Exchangeable: 8 mL of magnesium chloride solution (1 M $MgCl_2$, pH 7.0) was added and agitated for 1 hr at room temperature.

ii. Bound to Carbonates: 8 mL of 1 M sodium acetate (NaOAc) adjusted to pH 5.0 with acetic acid under continuous agitation for 5 hr at room temperature.

iii. Bound to Fe-Mn Oxides: 15 mL of 0.04 M $NH_2OH{\bullet}HCl$ and 5 mL acetate (HOAc) was added. The tubes were maintained at 96 ± 3 °C for 5 hr with occasional agitation.

iv. Bound to Organic Matter: 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3 with occasional agitation at 85 ± 2 °C for 2 hr. 3 mL of 30% H_2O_2 (pH 2 with HNO_3) was then added and the samples were maintained at the same temperature for another 3 hr with occasional agitation. Once cooled, 5 mL of 3.2 M ammonium acetate (NH_4OAc) and 1 mL HNO_3 was added. The sample was diluted to 20 mL and shaken continuously for 30 minutes.

v. Residual: The sum of the arsenic levels in the first four steps was subtracted from the total arsenic levels obtained by NAA.

5. Leachate Tests

Leachate tests were carried out following the procedure set out by the Ontario Ministry of Environment and Energy (MOEE), which sveral decades of acid rain

(MOEE, 1990). This analysis was used to aid in the determination of the stability of the arsenic within the tailings and sediment.

The first step of the process was to obtain the wet/dry ratio of the samples. The equivalent of 40 g dry weight of each sample and 640 mL of distilled water was measured into 1 L I-Chem™ bottles. The samples were tumbled for 15 minutes, and then the pH was adjusted to 5.0 ± 0.2 by adding 0.5 M acetic acid. The samples were agitated in a leachate box at 10 rpm for 24 hrs with the acidification being repeated after 1, 3, 6, 22 and 24 hrs with the total volume added not exceeding 160 mL. Additional distilled water was added to raise the volume to 800 mL. Prior to analysis by AA, the water was filtered through .45 micron filters.

V. METHOD APPLICATION

A. XRF Calibration

Similar to NAA, XRF has the benefit of analyzing solid samples without the need for a dissolution stage. Values are obtained through ionization of an inner shell orbital electron by X-ray emission. The atom becomes unstable when the vacancy is created. An outer shell electron moves towards the nucleus and replaces the displaced electron. This process leads to the release of excess energy in the form of a secondary "fluorescence" X-ray photon. The wavelength of the emitted energy is representative of the element and the intensity is a measure of the elements concentration (Potts and Webb, 1992)

The use of a portable x-ray fluorescence (XRF) device for analytical purposes has increased in popularity in recent years. When compared to traditional methods for inorganic element analysis such as AA or NAA, the XRF has certain distinct advantages. The XRF is very transportable since it can be contained within a large suitcase. The analysis is nondestructive, and it can be performed *in situ* on a variety of elements, over a wide range of concentrations, and in a rapid manner. All of these factors help reduce the cost of analysis (Piorek, 1990).

Calibration is required in order to ensure reasonable accuracy before a XRF is used in the field. The preparation of calibration samples must ensure that the expected range of contaminants is covered. Ideally, they should have physical characteristics similar to the samples to be analyzed. For *in situ* use, clean soil with similar physical characteristics to the contaminated site is normally collected, dried and sieved to remove the large particles. It is then spiked with the metals of concern covering any existing criteria concentrations (Piorek, 1990).

In the case of this study, *in situ* analysis was not feasible since most samples were sediment samples. Two sets of calibration standards were created to examine the effectiveness of the XRF for arsenic determination. Sodium metaarsenite from ($AsNaO_2$ - 98%) supplied by Aldrich Chemical Company, Inc. was dissolved in dissolved water to create a 20 000 ppm solution. This solution was used to spike the samples to the desired concentration.

The first set used silica sand and was chosen because the XRF bases its calculations on a silica matrix. The range of the calibration samples was from 150 ppm to 10 000 ppm. The lower limit was chosen based on the reported detection limit of 120 ppm (Piorek, 1990) and general knowledge of XRF operating efficiency at ESG. The upper limit was chosen to encompass the maximum expected value of arsenic levels in the sediment and tailings.

The second set of standards used Yellowknife River sediment from sample location #1. It was chosen because of the low arsenic concentration and the availability of sediment from this location. Four calibration samples were developed from 1000 to 5000 ppm. Figure V-1 shows the calibration curve for both sets of standards.

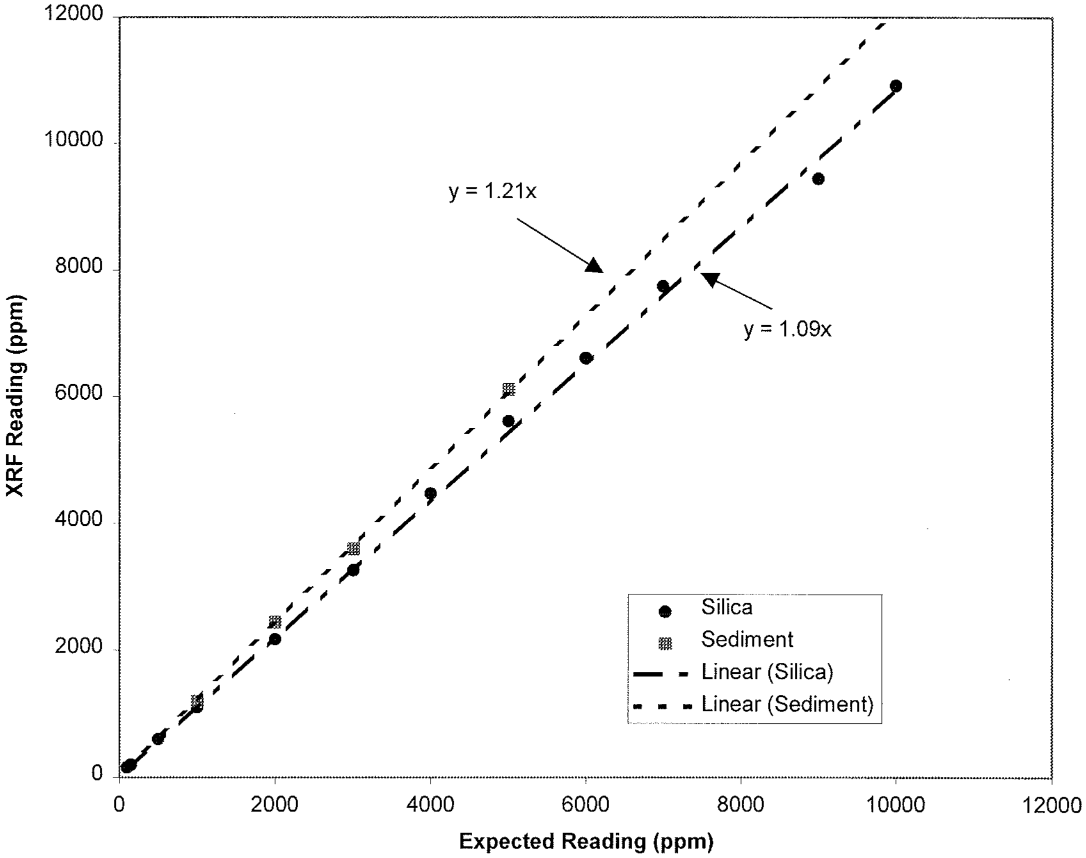


Figure V-1: Calibration of XRF

The XRF determination of the concentration of arsenic is linear over the range from 150 ppm to 10 000 ppm. Therefore, any error that would occur due to the method of analysis would appear to be constant throughout the range of concentrations found at this study site.

The difference between the slopes could be due to sample matrix effects caused by differences in the physical characteristics of the samples and differences in the concentrations of interfering elements. The slope determined for the silica sand standard is closer to one than the slope for the sediment standard. XRF analysis is based on a pure silica matrix, and would likely explain the difference between the slopes. The sediment standard also contains a number of other elements, which may have increased the intensity of arsenic measured by the detector (Duffy, 1998).

B. Comparison of XRF with NAA and AA

A correlation plot was produced in order to compare the arsenic results obtained by XRF with those obtained by NAA and AA. A total of 36 samples were examined for the XRF/NAA comparison and 17 samples for the XRF/AA comparison (Figure V-2).

It is readily apparent that a correlation exists between XRF and NAA when compared with the results obtained by using AA (Figure V-2). The relationship between NAA and XRF were not found to be significantly different (Paired t-test = 1.672, p = 0.103, df = 35). However, a significant difference was found (Paired t-test = 5.442, p =0.000, df = 17) between AA and XRF.

The correlation between the NAA and XRF results is also shown by their correlation coefficients. The R^2 value shown (Figure V-2) is the coefficient of determination, which is a measure of the proportion of variance. The positive square root of this value is the multiple correlation coefficient, R (Zar, 1984). Correlation plots with slopes near 1.00 and correlation coefficients of greater than 0.90 indicate good correlation between two analytical techniques (Harding and Walsh, 1990). The R values are 0.9655 for the NAA/XRF comparison, and 0.8437 for the AA/XRF comparison.

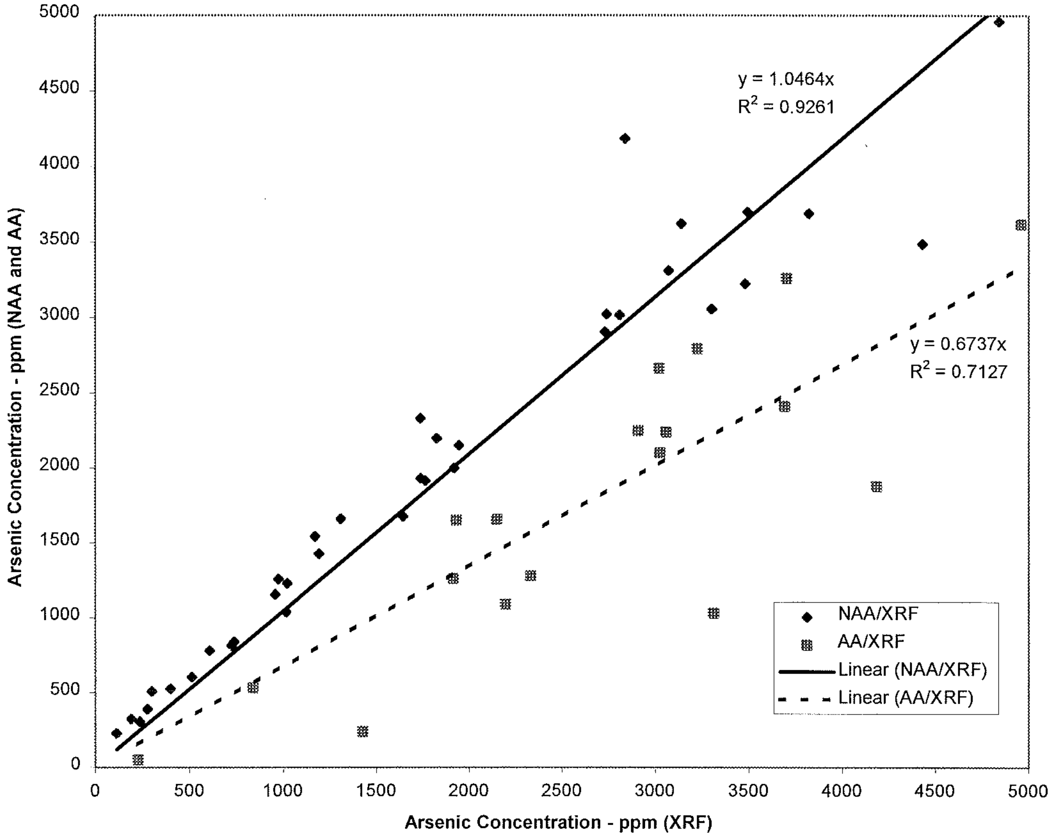


Figure V-2: XRF vs. NAA and AA for arsenic concentrations

The variation in obtained results may be due to the fact that the extraction procedure in AA analysis does not achieve 100% extraction of the metals as some are tightly bound within the soil matrix. The extracted metals are generally considered to be the more bioavailable metals within the sample. The total amount of a metal can be readily determined with both XRF and NAA since no extraction is required.

The accuracy of the XRF for arsenic analysis was further confirmed by the analysis of the standard reference material, PAC-1, which has a certified value for arsenic of 211 ± 11 ppm. It was analyzed for arsenic five times giving an average concentration of 192 ppm with a standard deviation of 21. The average relative standard deviation for arsenic was found to be less than 3% (Table X-14 in Appendix B).

The XRF was found to be an effective analytical technique for the determination of arsenic in heavily contaminated areas where concentrations exceeded 100 ppm. In comparison to both the AA and NAA, the time required for arsenic analysis of soil samples is greatly reduced. Turn around times as short as 24 hrs are possible with the

XRF. Since the analysis can be done on site, the need for re-visit can be reduced or eliminated as the contaminated site can be delineated in the field. The combination of these factors can result in a considerable reduction in the cost of an arsenic investigation program.

However, the approximate $80 000 cost of a TN Spectrace 9000 XRF or the monthly rental rate of $9000 must be taken into account in the determination of potential cost savings. An AA can cost in the range of $30 000 with the cost analysis of a sample at ASU being $25 for the extraction, $10 for the first element and $5 for each additional metal. NAA analysis at RMC costs a minimum of $40, but allows for multi-element analysis for this one price. Therefore, a cost benefit analysis is required prior to the selection of the analytical method. The location of the site, whether it is remote or is a local field site, needs to be considered as well.

VI. RESULTS AND DISCUSSION

There are four possible sources of arsenic in the area of Yellowknife Bay: 1) natural, 2) aerial, 3) particulate and 4) dissolved. Aerial deposition of arsenic in the area surrounding the Giant Mine is ongoing, albeit at lower levels than once occurred. The source of particulate arsenic could be incomplete settling of arsenic within the effluent treatment process, entrainment of particulates in water runoff from the tailings areas and/or bulk displacement of contaminated sediments. Dissolved arsenic may originate from the effluent discharge and/or the leaching of arsenic from the tailings areas.

Naturally occurring arsenic within the Yellowknife area is reported to be in the range of 2 to 10 ppm in rock with concentrations up to 3% in gold bearing ores (Mudroch *et al.*, 1989). There has been considerable debate regarding the sources of arsenic, natural vs. anthropogenic and one goal of this thesis was to differentiate between the two.

A. Surface Water

The concentration of arsenic in water (Figure VI-1) was determined at a number of locations (Map VI-1 and VI-2). The arsenic concentration of the tap water sample (Figure VI-1), obtained from a tap at Environment Canada's laboratory in Yellowknife, was 0.8 ppb, which is far below the current Canadian drinking water criteria of 50 ppb and also below the lower level of 2 ppb that the USEPA is considering. Throughout most of Yellowknife Bay, the concentration is below 10 ppb. All data are presented in Table X-7 of Appendix A.

Arsenic concentrations within Baker Creek and the outlet area (#4) were found to exceed the drinking water criteria. The elevated levels at locations #24 (52 ppb) and #29 (175 ppb), upstream from the effluent discharge, could be due to the elevated levels of naturally occurring arsenic in the area and/or the effects of the aerial emissions. The possibility of seepage and/or surface runoff of contaminants from the Northwest Pond could also influence the high concentration of arsenic in the water at sample #29.

The arsenic levels in Baker Creek remain above 100 ppb arsenic from sample location #20 near the effluent discharge to sample location #22 at the end of the creek. This shows that dissolved arsenic being discharged by the mine is reaching Yellowknife Bay by means other than bulk displacement of sediment. At sample location #4 in the

Bay, the concentration is less (55 ppb at surface & 2 ppb at 3 m) than what it was throughout the creek. This reduction in concentration is likely due to a combination of precipitation of the arsenic and dilution upon entering the Bay.

The only other location of high arsenic concentration within the water column is within the Beach Tailings Area at sample location #27 (67 ppb). This sample was collected close to the shore where the water was 0.5 m deep. This elevated concentration is possibly due to the influence of leachable tailings in the Beach Area.

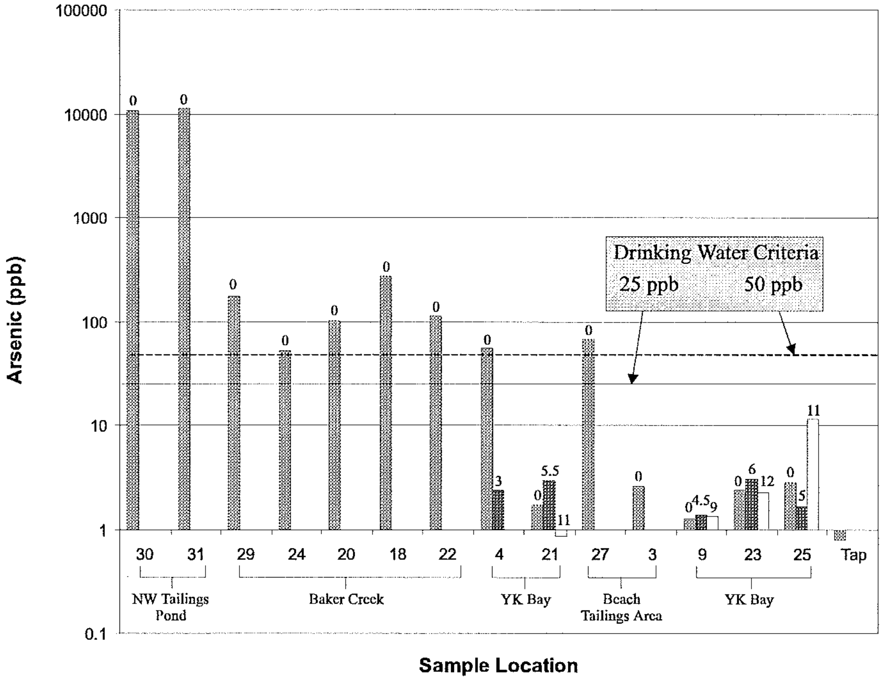


Figure VI-1: Arsenic concentrations in surface water samples. Sampling depths, in meters, are indicated. A value of 0 indicates a surface water sample.

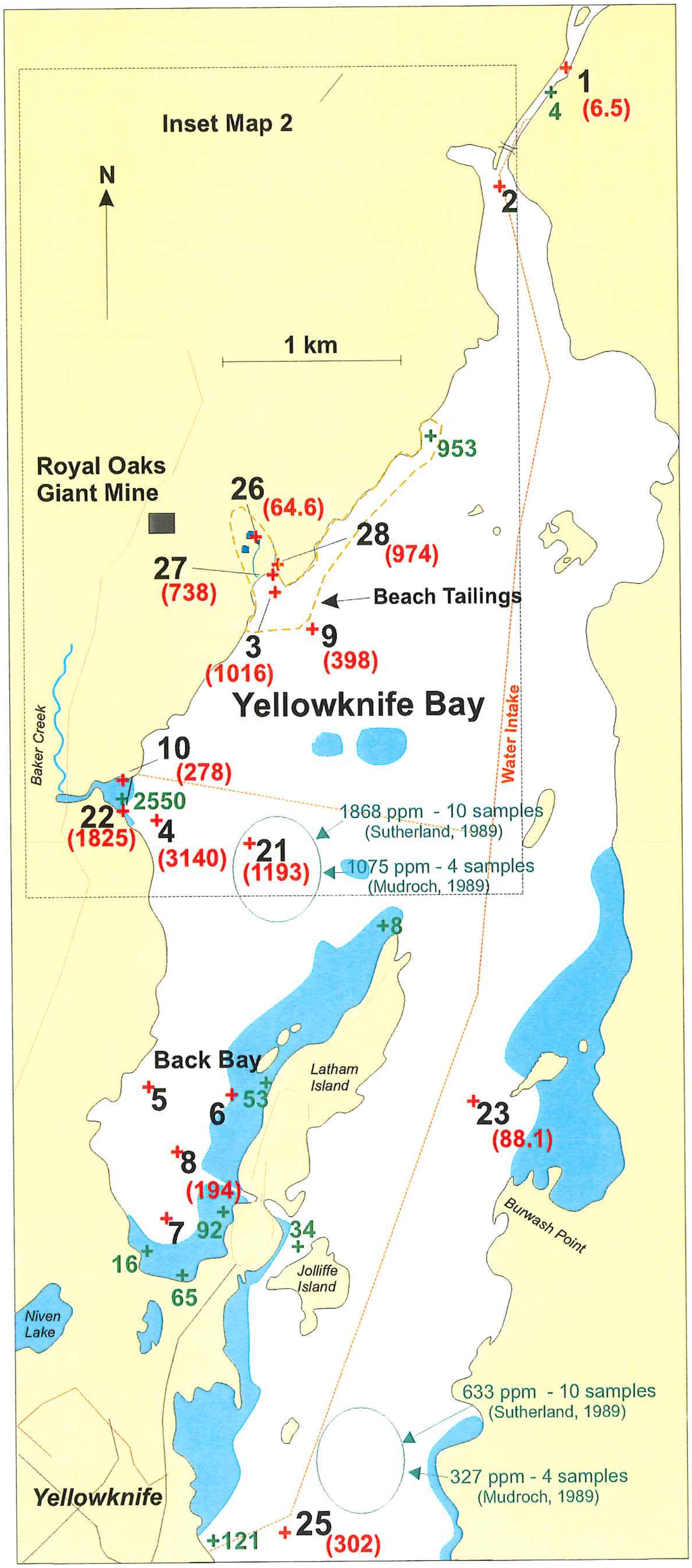
The lower levels of arsenic within the water column of Yellowknife Bay found during this study are similar to the results obtained by Sutherland (1996). The only high value that they found was at a similar location as sample location #22. They obtained samples four times throughout the year with an average concentration of 70 ppb. The sample obtained during March greatly lowered this average as it had a concentration of only 0.4 ppb arsenic. The mine does not discharge effluent during the winter, which explains the low concentration of arsenic found in March.

B. Sediments

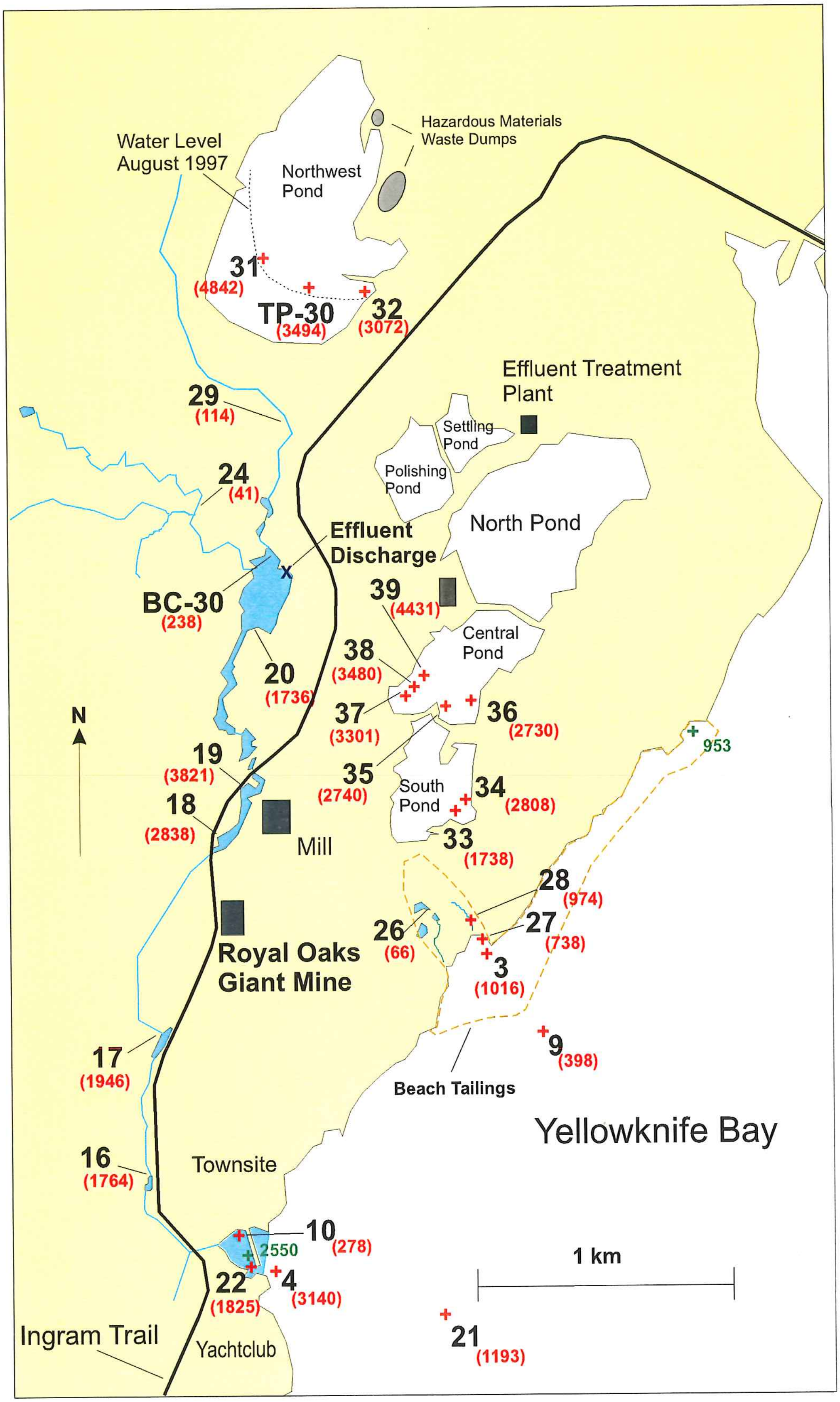
Map VI-1 and VI-2 indicate sampling locations and, in parenthesis, the arsenic concentrations in sediments from grab samples or the 0-5 cm section of cores collected during the summer of 1997. The values shown in green are from previous studies (Mudroch, 1989; Sutherland, 1989; Jackson *et al.*, 1996).

These samples were also analyzed for 13 elements (Table VI-1). The probable effect level (PEL) and the severe effect level (SEL) set by Environment Canada and the MOEE are included in Table VI-1 for comparison with the determined concentrations. The concentrations which exceed the PEL and/or the SEL are in italics. The arsenic concentrations of the surface sediments and tailings ponds are shown in Figure VI-2.

A marked difference from previous studies was the number of samples collected from the different tailings areas, including the old tailings area, hereafter referred to as the Beach Area. This also marks the first known time that there has been a detailed investigation of contaminant levels in Baker Creek.



Map VI-1: Sample locations from Yellowknife Bay. Arsenic concentrations from surficial sediments (0-5cm) for this study are indicated in red. Values in green are results from previous studies (Mudroch, 1989; Sutherland, 1989; Jackson *et al.*, 1996).



Map VI-2: Sample locations from Royal Oak Giant Mine. Arsenic concentrations from surficial sediments (0-5cm) for this study are indicated in red. Values in green are results from previous studies (Jackson *et al.*, 1996).

Table VI-1: Surface sediment concentrations (ppm) of various elements.

Sample	As	Fe	Mn	Zn	Cu	Ni	Co
Environment Canada – Probable Effect Level							
PEL	17			123	197	35.9	
MOEE – Severe Effect Level							
SEL	33	40000	1100	820	110	75	
New Tailings							
30	*3494*	*82200*	*1240*	*365*	*266*	*90*	35
31	*4842*	*96400*	*1246*	*600*	*537*	*118*	58
32	*3072*	*78800*	*1275*	*346*	*148*	*81*	36
Old Tailings							
33	*1738*	*65500*	*1147*	*157*	54	*60*	27
34	*2808*	*69970*	*1285*	*379*	*234*	*66*	20
35	*2740*	*72800*	*1352*	*263*	64	*81*	30
36	*2730*	*63600*	*1190*	*206*	*474*	*67*	24
37	*3301*	*73400*	*1239*	*185*	39	*91*	36
38	*3480*	*82800*	*1165*	*343*	*320*	*67*	28
39	*4431*	*76000*	*1314*	*182*	70	*85*	40
Con Mine Tailings							
44	*1919*	*82100*	1086	*328*	*263*	*71*	27
45	*1643*	*75800*	*1130*	*252*	102	*69*	29
Beach Area							
3	*1016*	38800	1080	108	24	28	7
26	*65*	36600	512	74	29	*44*	13
27	*738*	35800	*1256*	115	22	28	5
28	*974*	38000	*1129*	126	37	30	9
Baker Creek							
24	*41*	24500	329	99	15	23	6
29	*114*	37600	586	62	26	*38*	15
BC-30	*238*	30800	320	101	61	32	8
20	*1736*	19700	168	*259*	*1583*	*205*	26
19	*3821*	*51660*	695	*255*	*288*	*148*	54
18	*2838*	31000	798	*245*	*249*	*227*	101
17	*1946*	35500	412	*125*	90	*71*	26
16	*1764*	*41100*	495	*260*	367	*137*	137
10	*278*	29400	239	*183*	42	*60*	19
22	*1825*	39200	412	*331*	*392*	*89*	28
Yellowknife River and Yellowknife Bay							
1	6	34700	399	50	17	27	9
9	*398*	*40900*	482	95	42	*38*	15
4	*3140*	*43000*	424	*286*	*270*	*94*	37
21	*1193*	*41300*	*1610*	*149*	*312*	*62*	20
8	*194*	*41400*	540	*184*	*224*	*40*	10
23	*88*	*40600*	1000	107	54	*54*	10
25	*302*	*47300*	1057	148	100	*58*	14

Table VI-1 (cont'd): Surface sediment concentrations (ppm) of various elements

Sample	Sb	Au	K	Na	Ca	La
New Tailings						
30	413	1.2	18200	4758	68810	9
31	432	1.4	13500	3962	61460	9
32	326	0.9	14700	4859	68150	8
Old Tailings						
33	126	1.1	10200	3126	68040	5
34	245	1.1	18500	4219	64730	7
35	247	1.1	18500	3508	70290	6
36	239	1.6	15900	6028	68800	5
37	89	1.6	11500	4002	65000	8
38	354	16.9	13000	5151	68300	8
39	300	3.1	13400	5807	62120	9
Con Mine						
44	23	0.9	12700	4850	69110	20
45	20	0.8	10000	7980	73630	14
Beach Area						
3	39	3.4	9300	3370	68850	4
26	5	0.05	25200	13010	27020	49
27	46	1.8	9165	3143	74510	4
28	67	1.7	10100	3003	73580	4
Baker Creek						
24	1	0.007	17200	19290	15470	25
29	5	0.022	22300	16810	15010	42
BC-30	205	0.35	25000	18620	17320	39
20	182	6.3	18500	17280	17490	28
19	301	13	29200	11500	24520	24
18	441	23	18500	8786	24560	22
17	122	2.7	21600	17820	19990	28
16	208	5.9	18300	12660	20300	25
10	63	1.9	19100	15200	12820	36
22	235	3.9	5659	4846	20010	20
Yellowknife River and Yellowknife Bay						
1	0.4	<0.004	26100	17230	12040	43
9	19	0.7	22800	17520	12990	38
4	201	4.7	25000	16140	18400	27
21	66	1.2	25900	14470	12480	37
8	33	1.4	23400	16900	13190	42
23	5	0.3	23300	15880	13430	45
25	15	0.7	22400	14400	12780	45

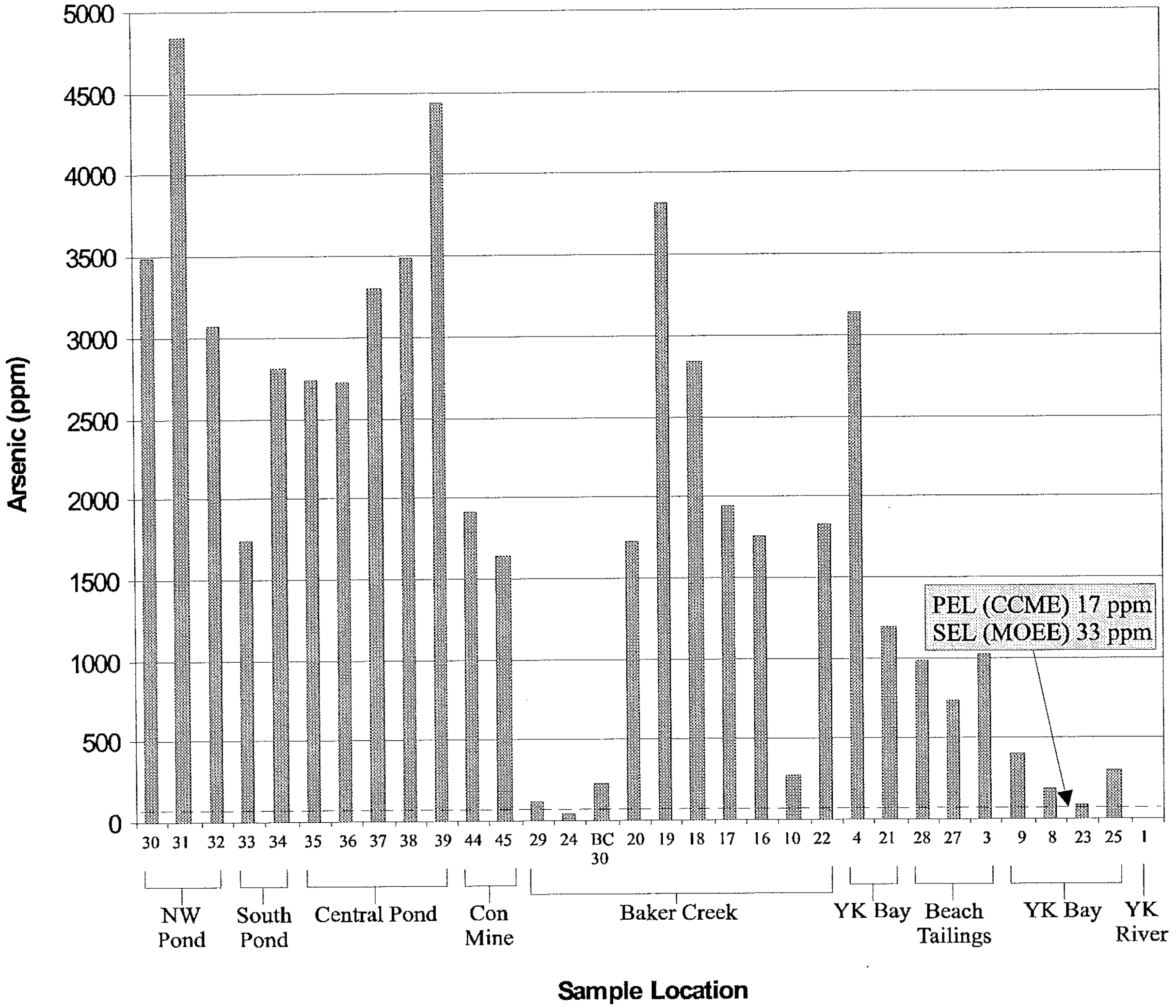


Figure VI-2: Arsenic concentrations in surface sediments and tailings samples.

1. Yellowknife River - #1

Sample location #1 has not been affected by the anthropogenic discharge of contaminants. Particulate transport and/or dissolved arsenic from the mine will have no effect on this location. The effect of aerial transport will be minimal as sample location #1 lies to the northwest of the total arsenic exceedance area predicted by the aerial transport model (Dillon, 1995).

A number of the elemental concentrations at this location are the lowest found. The arsenic concentration of 6 ppm correlates closely with the 4 ppm reported by Jackson *et al.* (1996). These concentrations are representative of background locations within the Yellowknife River, but not for Yellowknife Bay. The Bay has a number of other inputs than Yellowknife River and may be located in a different geological area.

2. *Baker Creek*

Sample results are presented and discussed beginning with the sample upstream of the effluent discharge (#24) and proceeding to the end of Baker Creek (#22). The sample locations are found on Map VI-2.

a) Baker Creek Background - #24 & #29

Sample locations #24 (Baker Creek) and #29 (Trapper Creek) reflect background concentrations similar to those found at sample location #1 other than arsenic (41 ppm and 114 ppm for #24 and #29). Both locations are upstream of the effluent discharge. This could be explained by higher concentrations of naturally occurring arsenic in this area and/or the increased effect of aerial emissions of arsenic because of the proximity to the roaster.

The levels of contaminants at sample location #29, situated below the man-made dam of the Northwest Pond, indicates that this area may not have been affected seepage and/or surface run-off of contaminants from the tailings. In recent years, construction of the tailings ponds and the stabilization of the creek upstream has occurred in this area. It is possible that the sample taken is not natural sediment, but consists of materials used for this construction. Sample location #24 has not been affected by any construction in the direct vicinity. However, sample locations #24 and #29 exceed the arsenic PEL and SEL.

b) Baker Creek Pond - # BC-30 & #20

Sample location #BC-30 has low concentrations of all metals except antimony and arsenic. Sample location #20 contains higher levels of arsenic, copper and nickel compared to the background samples. The SEL was surpassed for these three contaminants reflecting the effects of the effluent discharge. The arsenic level obtained here (1736 ppm) is consistent with the majority of the surface samples collected throughout the rest of Baker Creek. It is apparent that some of the arsenic discharge is settling out either by the settling of particles and/or by the adsorption/co-precipitation with iron and manganese oxides. The concentration of copper (1583 ppm) is the highest copper level recorded, including the tailings samples. It is possible that the majority of the copper found within the effluent discharge is settling into the sediments immediately after discharge. This may indicate that the arsenic within the discharge is not in the dissolved form. The concentration of nickel is 205 ppm and the results show that nickel concentrations decrease as the distance from the effluent discharge increases. Antimony at 182 ppm is equivalent to the average concentration determined throughout the creek. The concentration of gold at this location of 6.3 ppm is indicative of the areas influenced directly by the effluent discharge. The upstream sample locations #24 and #29 contain very low levels of gold in comparison to the remainder of the creek.

c) Mill Samples - #18 & #19

This area is affected by more than just the flow of contaminants from upstream. In May 7, 1991, roughly 3000 gallons of sludge containing arsenic, cyanide, copper, lead, nickel, zinc and other chemicals was discharged into the area of the creek to the west of the mine, due to operator error. Royal Oak Mines was fined $5000 for the incident (Saywell, 1992). The results of this spill can be seen at sample locations #18 and #19, which have the highest arsenic, antimony and manganese levels throughout the creek. In addition, gold concentrations were found to be 23 and 19 ppm for sample locations #18 and #19, respectively. The highest gold concentration for the rest of the creek is 6 ppm at sample location #20. This is much higher than the tailings samples, where all but one sample has less than 4 ppm gold.

d) Downstream - #16 & #17

At both of these locations, the arsenic levels are in the range of surface concentrations within the creek (1700 to 2000 ppm). Sample location #17 differs from other creek locations in that it has a low copper concentration of 90 ppm.

e) Baker Creek Marsh - #10 & #22

Even though these two samples are close in proximity, it is apparent that there are differences in metal concentrations. In all cases, sample location #10 has lower levels of metals than does sample location #22. This can possibly be explained by the fact that the majority of water flows through the open channel past sample location #22 and into Yellowknife Bay. There is negligible movement of water in the location of sample location #10 as it is thickly covered by horsetail. The plant growth in this area far exceeds what is found at any of the other sample locations. It is possible that there is a significant uptake of metals by horsetails or that deposition simply does not occur in this area.

Sample location #22 shows that a number of contaminants are making their way down through Baker Creek from the point of effluent discharge. This could possibly be due to the contaminants being carried within the water, bulk movement of contaminated sediments, and continual redistribution of arsenic from upstream sediments. Good correlation was obtained with the results obtained by Jackson *et al.* (1996). In approximately the same location, they found 2550 ppm comparable to the 1825 ppm observed in this study.

3. *Yellowknife Bay*

a) Yellowknife Bay: Beach Area - #3, #9, #27 and #28

From both visual inspection and analytical results, it is clear that sample locations #3, #27 and #28 are composed of mine tailings. Sample location #9 consists of natural sediment, whereas, the other sample locations #3, #27 and #28 do not contain any visible amounts of organic matter and are not clay-like in appearance.

Samples #3, #27 and #28 all contain very similar concentrations for all elements. They differ from the newer tailings in that they have lower concentrations of arsenic, iron, antimony, zinc, nickel and cobalt. However, their arsenic and manganese levels still surpass the SEL and PEL (Table VI-1). The fact that these tailings are situated on the shore and within Yellowknife Bay is a concern since they are in direct contact with the aquatic environment.

Sample location #9 appears to be influenced by the proximity of the Beach Tailings samples. Visual inspection of this sample reveals that this is not attributable to erosion of the tailings. It is more likely due to the redistribution of various elements, especially arsenic. The level of contaminants at location #9 is low in comparison to the remainder of the Bay, other than for iron and arsenic. The iron levels are similar to the concentration within the rest of the Bay. The arsenic level of 398 ppm is likely due to redistribution of arsenic from the Beach Tailings into the water column in the dissolved form followed by adsorption/co-precipitation with iron and manganese oxides at another location. Bulk transport of the tailings does not appear to have affected sample location #9. The sample location is also within the zone impacted by aerial emissions of arsenic.

b) Yellowknife Bay: near the creek outlet - #4 and #21

Sample location #4 has the highest arsenic concentration (3140 ppm) of the Yellowknife Bay sediment samples. This may be due to the redistribution of arsenic from the creek sediments followed by adsorption/co-precipitation and/or bulk transport of contaminated creek sediments; likely, it is a combination of both. Upon reaching the relatively stable waters of the Bay, the sediment particles would tend to settle out.

The surface concentration of arsenic appears to have diminished at sample location #21. The primary source of arsenic in this location is likely due to redistribution as opposed to bulk transport of sediments due to the increased distance from Baker Creek and the minimal current found within this area. The value obtained here is in the range of concentrations reported by Sutherland (1989) (1868 ppm) and Mudroch *et al.* (1989) (997 ppm).

It is evident from the concentrations found at these two sample locations that the flow of contaminants down Baker Creek is having an impact within the Bay. The antimony concentration of sample location #4 (201 ppm) is similar to that of the creek concentration. The same can be said for copper concentrations of sample locations #4 (270 ppm) and #21 (312 ppm). The manganese concentration (1610 ppm) at location #21 is higher than all other samples. The concentration of gold at sample location #4 (4.7 ppm) falls within the range of levels found throughout Baker Creek, while the 1.2 ppm of sample location #21 indicates that this location is affected by Baker Creek.

c) Yellowknife Bay: South of the creek outlet - #8, #23 and #25

The concentration of metals resulting from the Baker Creek outflow has diminished in these three samples. However, within Back Bay, high copper levels persist (224 ppm). Even though the arsenic concentrations are lower than in the Baker Creek outlet area, they continue to surpass the SEL and PEL. This is likely from a combination of aerial deposition and the redistribution of arsenic from the areas directly affected by Baker Creek.

4. Tailings Ponds - #30 to #39

The actual age of the tailings cannot be determined. However, it is generally accepted that the Beach Tailings are the oldest and Northwest Pond tailings are the most recent with the Central and South Pond's age lying somewhere in between (Schultz, 1998). All of the elements measured, with the exception of manganese, show an obvious trend; the more recent tailings contain higher concentrations.

5. Depth Profile of Sediments

The depth profiles of a number of cores have been determined in order to establish whether the concentration of contaminants decreases with depth. This information will help determine the background concentration of arsenic within Yellowknife Bay. These profiles are presented in Table VI-2 and Table VI-3. Sample location #1 was included in both tables as a basis of comparison for background concentrations. Table VI-4 is a summary of the depth profiles obtained within Yellowknife Bay by Sutherland (1989) and Mudroch *et al.*(1989).

The level of contamination decreases as expected at sample locations #18, #20, #21, #22 and #25 (Table VI-2). Only the core obtained at location #25 is deep enough to have reached a depth with a constant arsenic concentration, 116 ppm at 10-15 cm vs. 130 ppm at 15-20 cm. These values are in the range of concentrations determined by Sutherland (1989), which were 79 ppm and 85 ppm at the same depths (Table VI-4). The anthropogenic discharge of contaminants that have occurred within the last 50 years would appear to have affected the top 10 to 15 cm of the sediment.

The concentration of arsenic, iron, manganese, zinc and copper increased with increased depth at the sample location #17 in June. The concentrations decreased slightly with depth at sample location #17 in August. However, the arsenic concentration was still 5914 ppm at 10-15 cm in depth. This section of the creek may have been influenced by the upstream diversion of the creek to make way for an open pit mine. The bed of the creek in this section is covered with clay-like sediment (Photo IV-5), which may explain the presence of dead trees along the banks.

The concentrations of antimony, arsenic, iron and zinc at location #4 increase by a factor of at least two from the 0-5 cm section to the 5-10 cm section. The concentration of arsenic increased from 3726 ppm to 10 710 ppm at the 5-10 cm section. The increase in contaminants at depth could reflect a positive change in the environmental practices at the mine and their effects on Yellowknife Bay. The reason this was only seen at sample location #4 and not #21 may be because of the proximity of sample location #4 to Baker Creek. The bulk transport of sediments by Baker Creek likely results in a higher sedimentation rate at location #4. If this is the case, the reduction in contaminant level may be due to the improved environmental practices of the mine in recent years. The primary source of contaminants at sample location #21 is more likely redistribution by means of arsenic diffusion into the water column. Therefore, a reduction of the contaminant level carried by bulk transport will have little effect on areas of the Bay farther from Baker Creek since high concentrations of arsenic that are available for redistribution persist in the sediments.

Table VI-2: Depth profiles of sediment concentrations (ppm) of various elements determined by XRF.

Sample	Depth (cm)	As	Fe	Mn	Zn	Cu	Sb	K	Ca
1		104	28320	470	50	77	ND	29590	12040
4	0-5	3623	36100	847	309	737	192	24440	1808
	5-10	10710	62530	1070	986	343	1309	25460	33390
17 (June)	0-5	2150	28543	877	143	174	126	23280	19843
	5-10	4521	44290	1430	314	1220	28.3	23140	42520
17 (Aug)	0-5	7460	60390	1030	748	210	1074	26730	39340
	5-10	6397	60227	1333	678	213	1225	16927	5267
	10-15	5914	56600	1250	683	180	1040	19430	56530
18	0-5	4227	36133	1480	250	349	335	21123	25077
	5-10	793	23060	960	86	61	34	26970	12140
20	0-5	2332	18990	810	259	2193	179	21050	17490
	5-10	2225	20290	480	386	1802	267	23050	15100
	10-15	309	21100	510	75	125	59	23090	14220
21	0-5	1428	35340	3690	149	225	31	27090	12480
	5-10	610	36780	1430	256	192	81	29050	11300
	10-15	260	37660	1690	114	49	ND	27230	13060
22	0-5	2197	37390	1090	331	497	351	25500	20010
	5-10	1713	34520	1180	232	533	262	26450	18360
	10-15	206	26730	750	109	77	ND	28390	11870
25	0-5	509	40490	2690	148	104	30	27000	12780
	5-10	173	34340	1220	94	67	ND	28280	12020
	10-15	116	35930	960	75	77	39	28810	12420
	15-20	130	33920	660	101	41	ND	28680	11870
27	0-5	839	29410	1580	115	85	67	10720	74510
	5-10	812	28160	1490	69	28	70	9960	69360
	10-15	888	29550	1220	100	ND	72	10750	70120
	15-20	891	28220	1100	88	64	60	11920	59960
	20-21	865	30590	1690	109	ND	52	14210	63110

The concentrations of all elements throughout sample location #27 remain constant throughout the 21 cm of the core. This corresponds with the visual inspection of the core where it was apparent that the bottom of the tailings had not been reached.

Table VI-3 presents the results for two cores obtained at sample locations #7 and #22 which were cut at 0.5 cm increments for the first 10 cm and 1 cm increments thereafter. Sample #7 would appear to be deep enough to have reached background levels similar to those obtained at sample location #1. It is apparent that this location has not been affected by anthropogenic discharge to the degree of the rest of Yellowknife Bay. In addition, decreases in concentration of arsenic, zinc, antimony and gold are apparent at increased depth. The concentrations at 26 cm are almost identical to those obtained at location #1 indicating that the true background concentration within Yellowknife Bay may be similar to the concentration of the sediments at sample location #1. This is further confirmed by the similarity between the low arsenic concentrations found at depth at location #7 and the cores obtained by Mudroch *et al.* (1989), Table VI-4. The same can be said for zinc as the concentration of zinc found by Mudroch *et al.* averages about 110 ppm after the first 6 cm. The background concentration for arsenic at sample location #7 would appear to be 7 ppm.

Sample location #24 was included in Table VI-3 for comparison with sample location #22. The concentration of arsenic, iron, zinc, antimony and gold decrease with increased depth at location #22. A deeper core may provide a clearer picture of background concentrations. The concentrations of the elements other than iron would appear to be fluctuating up and down with no specific pattern as the depth increases. These concentrations may provide a range of possible background concentrations at this location. Regardless of the element, the concentrations at location #22 exceed those found at sample location #24. This may because of the Baker Creek runs through an area which contains naturally high concentrations of these elements. The background arsenic concentration for Baker Creek is likely in the range between the 41 ppm for sample location #24 and 104 ppm for sample location #22 at a depth of 13 cm.

Table VI-3: Depth profiles of sediment concentrations (ppm) of various elements determined by NAA. Depths are shown in centimeters after the sample number for the sediments at depth.

Sample	As	Fe	Zn	Sb	Au	K	Na	La
1	6.48	34700	92	0.39	0.0021	26100	17230	42.9
7-0.5	61.71	33700	153	15.5	0.987	22300	16960	39.92
7-3	84.88	27400	147	11.84	0.752	21700	20310	36.7
7-6	43.9	29000	102	4.74	0.194	23400	18870	41.43
7-8.5	22.22	30000	70	1.32	0.0048	23900	18660	44.62
7-14	10.31	30600	64	0.695	0.0056	23900	16640	44.48
7-20	6.6	30700	94	0.58	<0.0081	22900	18100	43.6
7-26	7	33200	109	0.53	<0.007	25500	17400	46.1
24	41	24500	67	1	0.007	17200	19200	25
22-0	1310	38200	197	132	7.541	19900	15370	28.54
22-1	1173	39700	224	151	4.62	20800	15890	29.1
22-2	1022	38100	183	128	3.174	19800	16820	30.23
22-2.5	956	37500	199	115	3.476	19300	16410	27.6
22-3	725	35800	185	109	2.503	21600	18330	32.9
22-3.5	514	31300	190	91.2	1.677	20500	17790	33.8
22-4	147.3	27600	88	54	0.497	20900	19460	36.69
22-4.5	58.4	24500	109	32.7	0.216	20300	18670	35.2
22-6	100.5	25500	108	25.52	0.375	22100	19520	36.82
22-8	65.07	23700	97	9.03	0.104	21700	20280	37.97
22-10	46.92	24700	98	6.03	0.084	22000	18580	36.24
22-13	104.3	28900	119	16.43	0.0289	23200	18420	40.86
22-16	70.32	28400	100	8.2	0.233	22800	18950	42.06

Table VI-4: Summary of depth profiles of sediment concentrations (ppm) of arsenic obtained by Sutherland (1989) and Mudroch *et al.* (1989).

Sutherland - 10 cores					Mudroch - 3 cores					
Depth (cm)	Near #21		Near #25		Depth (cm)	Near #21		Depth (cm)	Near #25	
	Mean	SD	Mean	SD		Mean	SD		Mean	SD
0-5	1868	552	633	147	**0-1**	1480	1159	**0-1**	440	142
					1-2	890	236	**1-2**	674	188
					2-3	1003	121	**2-3**	409	303
					3-4	953	280	**3-4**	78	28
					4-5	660	121	**4-5**	30	22
5-10	967	725	227	35	**5-6**	305	251	**5-6**	22	6
					6-7	139	62	**6-7**	20	3
					7-8	136	71	**7-8**	17	5
					8-9	126	58	**8-9**	22	3
					9-10	117	45	**9-10**	25	9
10-15	200	44	79	3	**25-26**	23	3	**20-21**	13	2
15-20	110	10	85	6				**27-28**	16	2

6. Principal Components Analysis - Surface Samples

To further analyze the data set in Table VI-1 consisting of 13 measured variables over 33 locations, a principal component analysis (PCA) was completed using the statistical program Systat 6.0.1. PCA allows for a statistical representation of numerous metal concentrations for each sample on a two dimensional plot which allows for the generation of a hypothesis from collected data (Pyle *et al.*, 1996).

Figure VI-3 shows the PCA plot with the variables (in this case metals) and each of the sample locations. The sample locations have been grouped into various categories. The sample sites contain the various samples collected in Yellowknife Bay, Back Bay and the Baker Creek samples upstream of the effluent discharge. The new tailings, old tailings and beach areas are samples collected from the Northwest Pond, the Central/South Ponds and the Beach Area along the shore of Yellowknife Bay, respectively. Two samples collected from the Con Mine Tailings were included as their own category. The Baker Creek samples consisted of the samples from the effluent discharge (#20) to the outlet area (#22).

In this PCA, the first two principal components were plotted. They combined to explain 45.9% and 25.6% of the total variance with eigenvalues of 5.973 and 3.322, respectively. The eigenvalues are direct measures of the amount of variance explained by their respective principal components (Pyle *et al.*, 1996). It is readily apparent from the plot that distinctive groupings of various sample locations did occur.

The tailings samples grouped together on the lower right portion of the biplot. The estimated age grouping of the samples is reflected here. For example, the Beach samples are found in tight group at the bottom followed by the samples from the South and North Ponds sitting slightly higher. Sample location #38 is found at the top of the old tailings sample group due to its high level of gold (17 ppm) compared to the other samples (1 to 3 ppm). The elemental characteristics of the tailings of the Con Mine correspond closely to those of the Giant Mine.

Sample locations #4, #21 and the Baker Creek samples formed a loose grouping in the upper portion of the biplot. Although they are not grouped as closely as the tailings samples, they are distinctive from the other samples. The looser grouping for these samples may be due to the proximity to the effluent pipe, the redistribution of contaminants, the effects of a large spill, or a number of different factors.

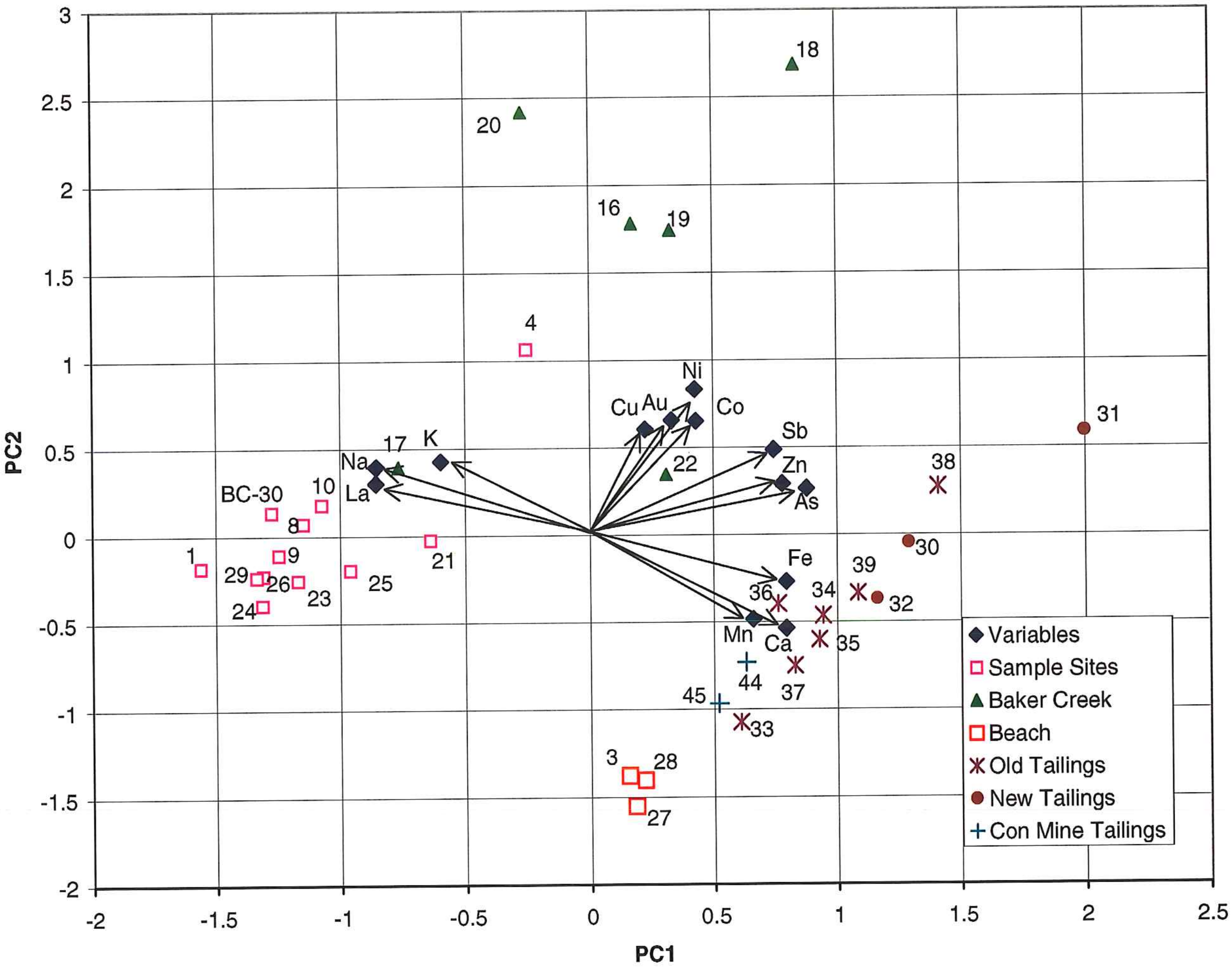


Figure V-1: Principal components analysis biplot showing sampling sites and chemical variables.

At the left side of the PCA plot, a collection of sample locations with lower concentrations of arsenic, zinc, copper, nickel, cobalt and antimony are found. The background sample taken at location #1 is located on the far left.

There would appear to be two distinct groups to the right of location #1. Sample locations #23, #24, #26 and #29 are characterized by lower concentrations of arsenic (41 to 114 ppm), gold (0.007 to 0.3 ppm), antimony (15 to 54 ppm) and zinc (62 to 107 ppm) with respect to the group formed by sample locations #8, #9, #10, #25 and #BC-30. This second group contains concentrations of arsenic from 194 to 398 ppm, gold from 0.35 to

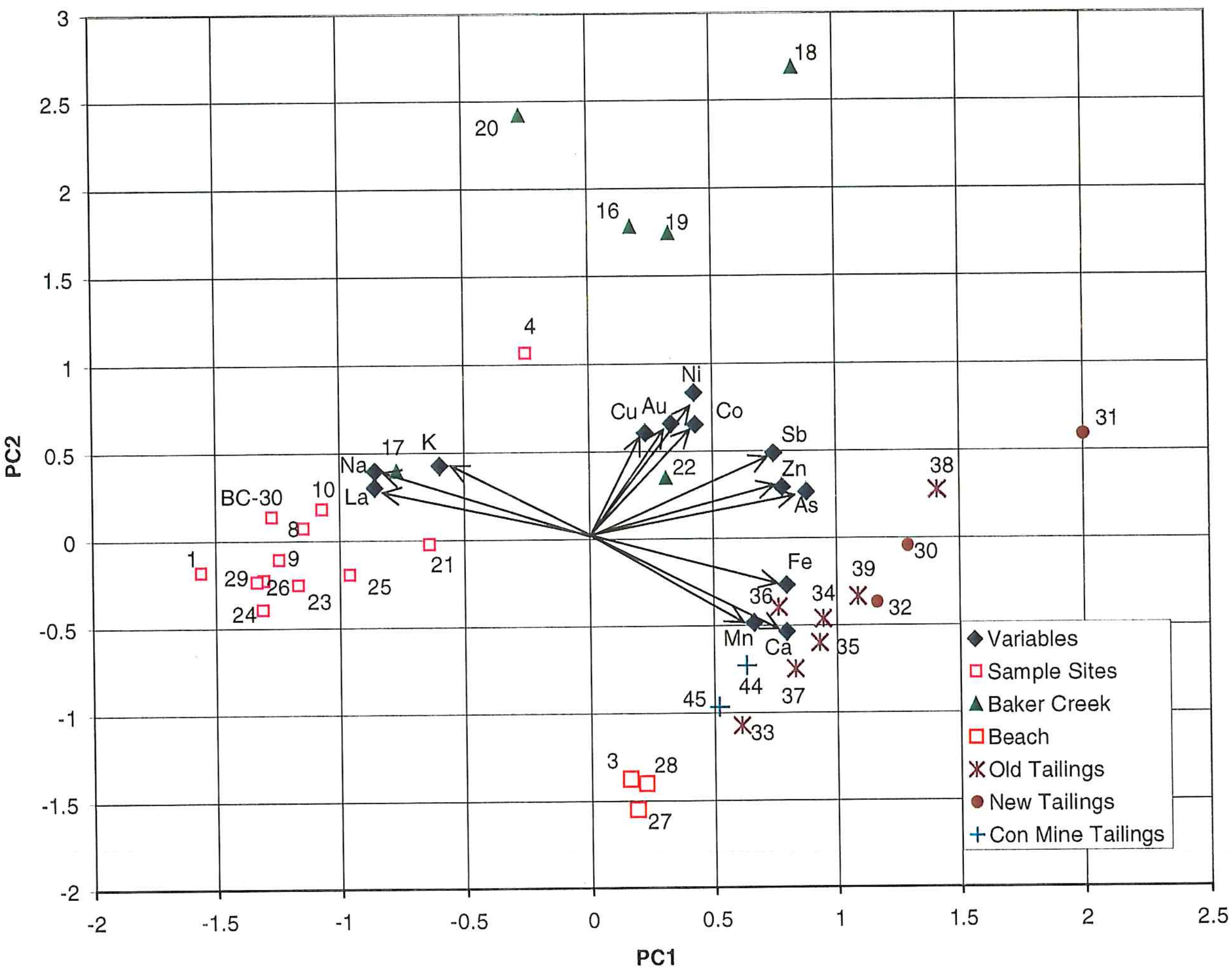


Figure VI-3: Principal components analysis biplot showing sampling sites and chemical variables.

At the left side of the PCA plot, a collection of sample locations with lower concentrations of arsenic, zinc, copper, nickel, cobalt and antimony are found. The background sample taken at location #1 is located on the far left.

There would appear to be two distinct groups to the right of location #1. Sample locations #23, #24, #26 and #29 are characterized by lower concentrations of arsenic (41 to 114 ppm), gold (0.007 to 0.3 ppm), antimony (15 to 54 ppm) and zinc (62 to 107 ppm) with respect to the group formed by sample locations #8, #9, #10, #25 and #BC-30. This second group contains concentrations of arsenic from 194 to 398 ppm, gold from 0.35 to

1.9 ppm, antimony from 15 to 205 ppm and zinc from 95 to 184 ppm. Samples locations #24 and #29 are both upstream of the effluent discharge. Location #23 contains a lower level of contaminants than does location #25 even though it is closer to the mine. It is unknown why sample location #26 contains low levels of contaminants considering its proximity to the mine and the fact that it is located within the Beach Tailings Area.

Sample location #9 contains the highest arsenic concentration (398 ppm) within this second group. However, it does have low antimony, copper and zinc levels. Despite its close proximity to the Beach Tailings Area (#3, #27 and #28), its elemental fingerprint is dissimilar to that of the tailings.

The PCA analysis provides information regarding the source of arsenic contamination within the area of Yellowknife Bay. As noted earlier, the source of arsenic may be natural, aerial, particulate or dissolved. The source of arsenic contamination within Baker Creek and Yellowknife Bay is anthropogenic in nature. There is a marked difference between the background sample location #1 and the two groupings just to the right with the samples locations found throughout Baker Creek and its outlet area into Yellowknife Bay (#4 and #21). The highly affected sample locations are from location #20 near the effluent discharge to location #21 in Yellowknife Bay.

The major source of anthropogenic contamination of the area would appear to be particulate arsenic and/or dissolved arsenic. A number of sample locations found closer to the mine have relatively low arsenic levels (i.e. #9, #24, #29 and # BC-30). If aerial deposition was dominant, the concentration of arsenic in sediments would decrease as the distance from the stack increases, but this is not the case. However, the aerial emissions have likely contributed to the high arsenic concentrations found in the surface sediments throughout Yellowknife Bay. Even with the improved effluent treatment plant, significant amounts of arsenic and other metals are being released within the effluent discharge as can be seen by the high levels of contaminants in the surface sediments.

7. *Principal Components Analysis – Depth Profile of Sediments*

The PCA was also used to investigate the characteristics of sediments at depth at a number of sample locations. The PCA in Figure VI-4 represents the depth profiles shown in Table VI-2 and Figure VI-5 represents the depth profiles shown in Table VI-3. Sample location #1 is shown to provide a basis for background concentrations. The PCA

also took into account the other surface sediment and tailings concentrations which are shown in Table X-5 and Table X-6 of Appendix A.

The first two principal components of the PCA in Figure VI-4 combined to explain 46.6% and 25.3% of the total variance with eigenvalues of 3.728 and 2.024, respectively. It is apparent that the locations (#18, #20, #21, #22 and #25), that the concentrations approach the background concentration of sample location #1 at increased depth. The grouping for sample location #27 is very small indicating that the 21 cm core consists of solely tailings material.

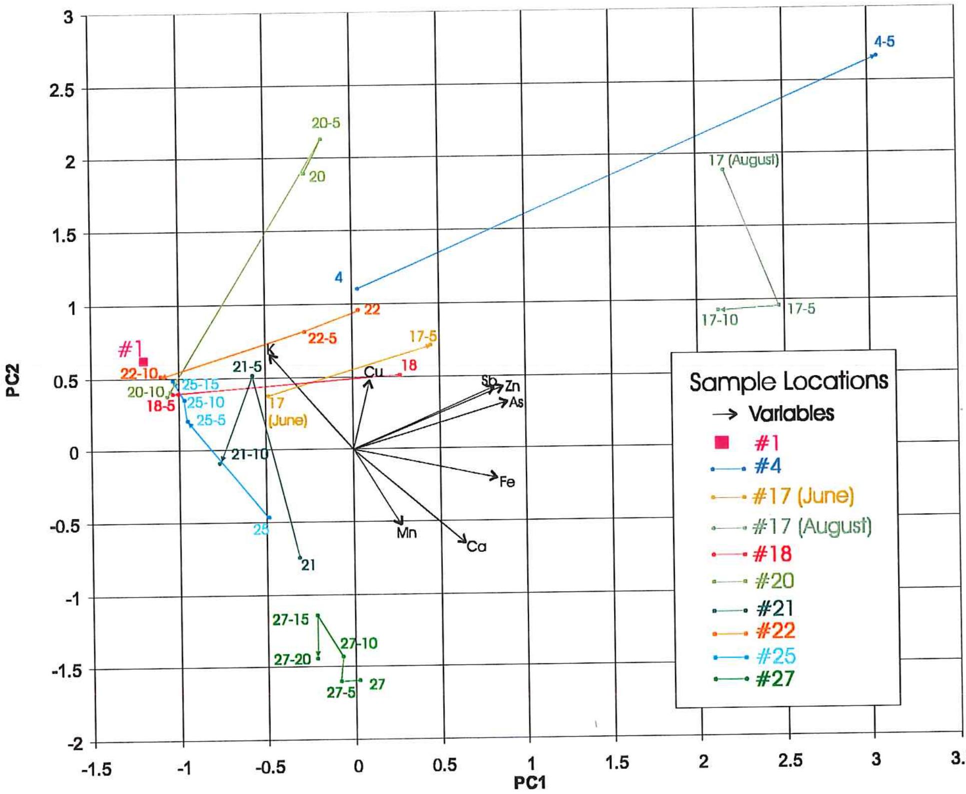


Figure VI-4: Principal components analysis biplot showing the characteristics of the sediments at depth and the chemical variables. Depths are shown in centimeters for the sediments at depth.

The PCA in Figure VI-5 demonstrates the depth profile for sample #7 located at the southern tip of Back Bay and sample #22 located near the end of Baker Creek. The

first two principal components of this PCA combined to explain 66.2% and 15.7% of the total variance with eigenvalues of 5.297 and 1.257, respectively.

Sample location #7 does not contain high levels of contaminants even at the surface. However, it is apparent from this PCA the levels decrease at increased depth. The section taken at 26 cm with an arsenic concentration of 7 ppm is very close to the location of sample #1.

Sample #22 compares well with the sample #22 in the previous PCA. The decrease in contaminant concentration from 0 cm to 4 cm is apparent as sample location #1 is approached.

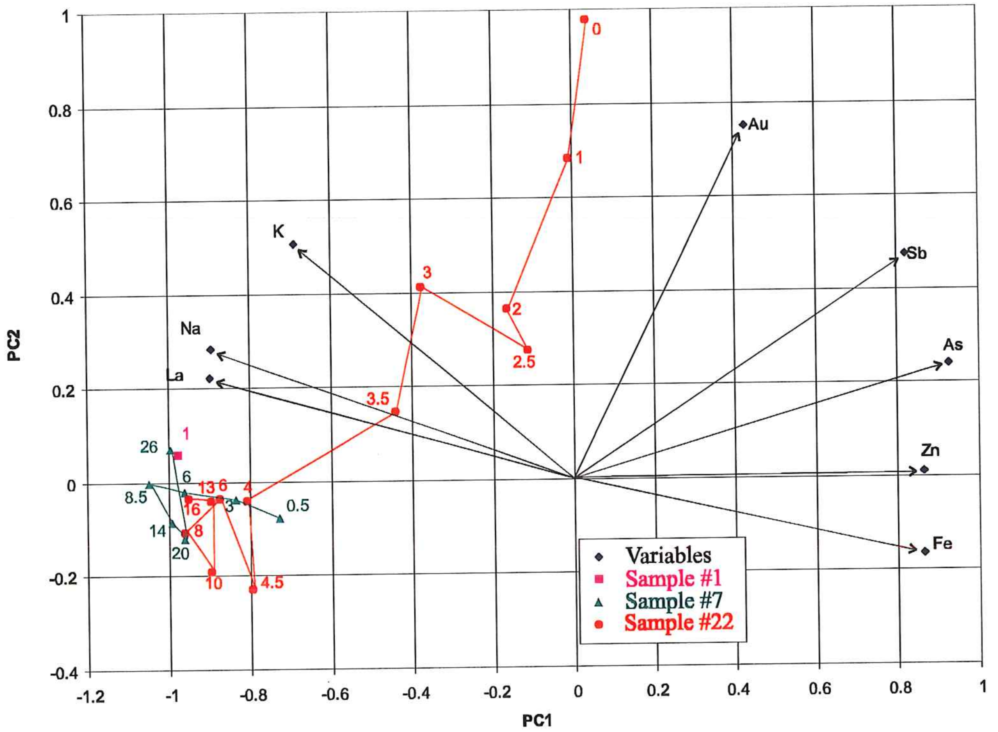


Figure VI-5: Principal components analysis biplot showing the profile of a core obtained at sample location #7 and #22 with depths shown in centimeters.

8. *Summary of Background Arsenic*

Sample location #1 was chosen to initially represent the possible background concentration of arsenic and other elements within the study area because it is the location to be the least affected by the anthropogenic discharge of contaminants. Its arsenic concentration of 6 ppm is the lowest determined in this study.

It would appear that the range for the background concentration of arsenic in Yellowknife Bay is between 7 and 25 ppm. This range of concentration was reached at a depth of 8.5 cm at sample location #7. The samples taken by Mudroch *et al.* (1989) reached this range by 25 cm sample location #21 and by 6 cm near sample location #25.

The background concentration throughout Baker Creek appears to be higher than the sediments of Yellowknife Bay likely due to the higher natural arsenic levels in the area of the creek. Sample location #24 upstream of the effluent discharge has an arsenic concentration of 41 ppm. The average arsenic concentration between 4.5 cm and 16 cm of sample location #22 located at the end of Baker Creek is 75 ± 30 ppm. The range of background concentrations within the creek appears to be 41 to 104 ppm.

C. Arsenic Load

The majority of the arsenic in the study area has been shown to be from anthropogenic sources. The regions with high arsenic concentrations due to mining operations include the baghouse dust stored in the mine shafts, the tailings ponds, the Beach Tailings Area and the sediments of Baker Creek and Yellowknife Bay. The amount of arsenic within the mine shafts has been provided by the Giant mine (Royal Oak, 1997), whereas the amount of anthropogenic arsenic in the other four areas has been calculated. These calculations were based on the determined dry density of the sediments or tailings and multiplying this value with the estimated average arsenic concentration and the volume of contaminated sediment/tailings.

1. *Tailings Ponds*

A summary of the amount of ore produced by the mine was provided by Stephen Schultz, the Superintendent of Environmental Services for the Giant Mine (Schultz, 1998). Over the course of 50 years, a total of 15 617 884 metric tonnes of ore have been milled at an average rate of 312 357 tonnes per year. The approximate 270 000 tonnes of baghouse dust, consisting of approximately 200 000 tonnes of arsenic trioxide, is subtracted from this total because it is currently stored in various mine shafts. The tailings ponds and Beach Area are estimated to contain 15 350 000 tonnes of tailings. For volume estimates, the Giant Mine estimates 1.2 tonnes of tailings per cubic meter with 44% of the volume as tailings and 56% of the volume being water.

To determine the actual amount of arsenic within these tailings, an average arsenic concentration of 2720 ppm was estimated (Table VI-5). This value is the average arsenic concentration of all of the tailings samples examined in this study, including the Beach Tailings. Using this value, there are an estimated 41 400 tonnes of arsenic within the tailings areas with a total volume of approximately 13 000 000 m^3.

Table VI-5: Area and average arsenic concentration of the Giant Mine Tailings Ponds.

Tailing Pond	Area (ha)	Avg. arsenic concentration (ppm)
Northwest Pond	42	3800
North Pond	27	Not sampled
Central Pond	11	3340
South Pond	11	2270
Polishing and Settling Pond	9	Not sampled
Beach Tailings	16	910
Total	116	2720

2. *Beach Area*

The total volume of tailings within the Beach Area is only a rough estimate at this time. The area covered by the Beach Tailings was determined using results from this study, a previous study (Jackson *et al.*, 1996) and a series of aerial photographs spanning the lifetime of the mine (Photo VI-1 and Photo VI-2).

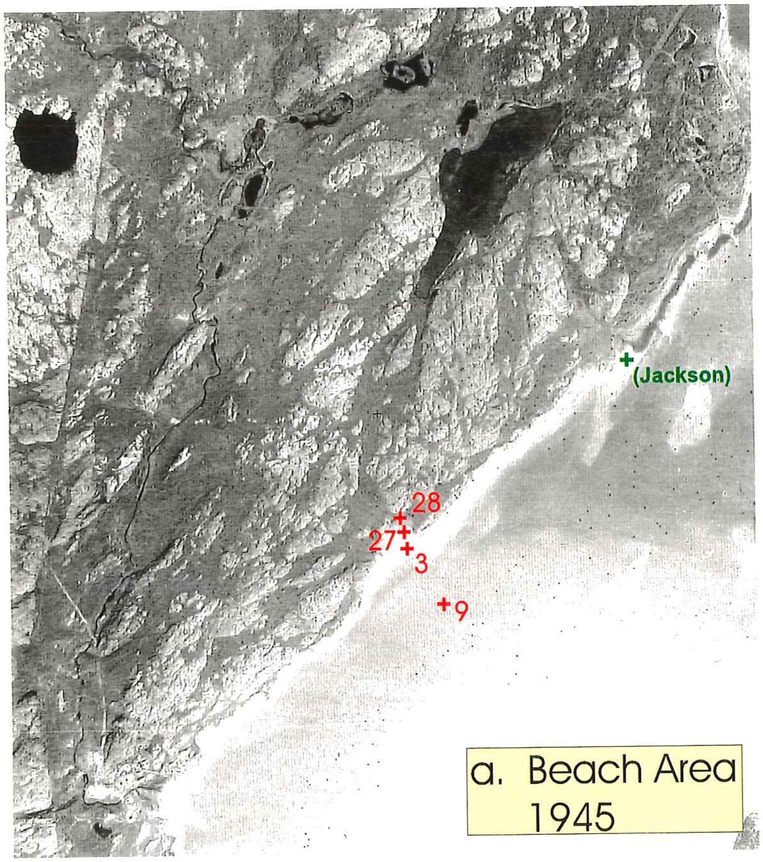
The surface sample PCA (Figure VI-3) demonstrated that sample locations #3, #27 and #28 were elementally similar and could all be considered part of the Beach Tailings Area. The results for sample location #9 demonstrated the maximum outer extent reached by the erosion of the tailings, directly offshore of the Beach Area. This was confirmed by inspection of aerial photographs.

The sample location reported by Jackson *et al.* (1996) to be from the "Old Giant Tailings Release Area" was found to have similar concentrations of a number of elements in comparison to the samples from the Beach Area (Table VI-1). The concentrations determined by Jackson *et al.* include 953 ppm As, 6.3 ppm Co, 19.8 ppm Cu, 16.3 ppm Ni, 101 ppm Zn, 39 100 ppm Fe and 1300 ppm Mn.

The location of this sample (Jackson *et al.*, 1996) is not believed to be an area of direct tailings release. This was confirmed by Stephen Schultz (Pers. Comm.) and by looking at the progression of the Beach Area in the aerial photographs. No pathway for direct tailings runoff from the ponds can be detected in any of the photographs. A possible explanation for the location of these tailings is the erosion of tailings from the Beach Area. The northern extent of the area affected by the erosion of the Beach Tailings was determined by Jackson *et al.*'s (1996) sample in conjunction with the aerial photographs.

In 1945 [Photo VI-1(a)], there is little evidence of development other than a small village located at the Baker Creek outlet. In its natural state, Baker Creek did not widen in the many locations it does currently. One feature to note is that the shorelines and shallow water to the north and south of the Beach Area are light in colouring. The lake, which is now covered by the Central and North Ponds, is also visible. The deposition of tailings along the shore of Yellowknife Bay is clearly visible in 1950 [Photo VI-1(b)] and it is believed that this marks the maximum extent reached by exposed tailings.

In 1966 [Photo VI-2 (c)], the tailings ponds are visible. The deposition of tailings in the Beach Area would appear to have stopped as they have been redirected to the tailings ponds. A large portion of the Beach Tailings have been eroded below the water level as the amount of visible tailings is greatly reduced. The erosion has likely resulted in the covering of the visible white area directly offshore of the Beach Area. In 1996 [Photo VI-2 (d)], the exposed Beach Tailings appear to be half the size that they were 30 years earlier and 20% of their size in 1950. An estimate of the area currently covered by the erosion of the Beach Tailings is shown with an area of 16 ha. The distance out from the Beach Area was determined by the location of sample #9 and the visible line within the water. The northern edge coincides with the sample reported by Sutherland (1989) and the extent reached by the visible white area.



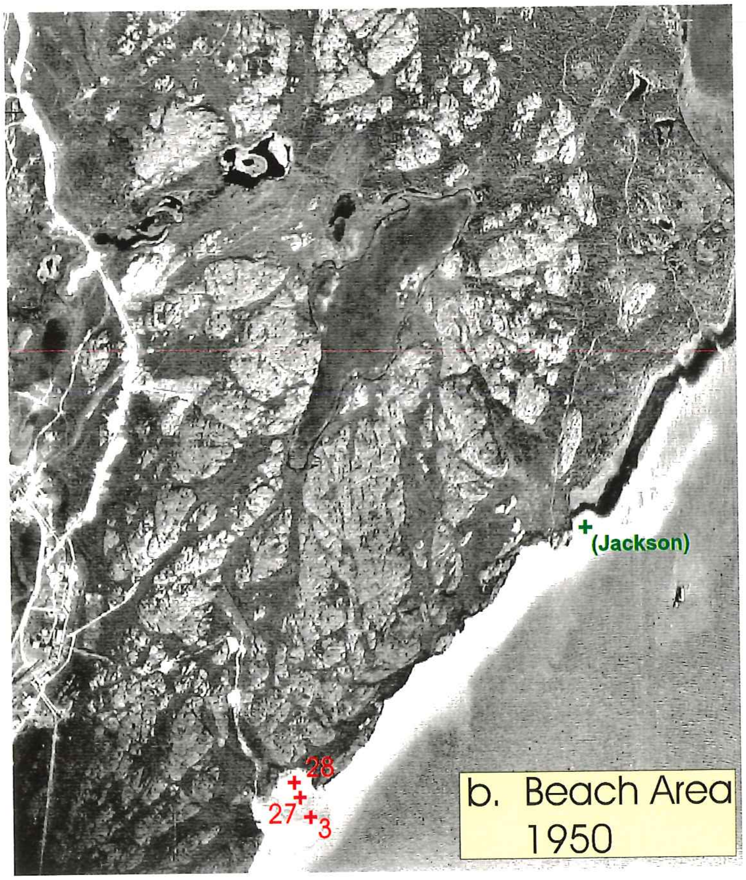
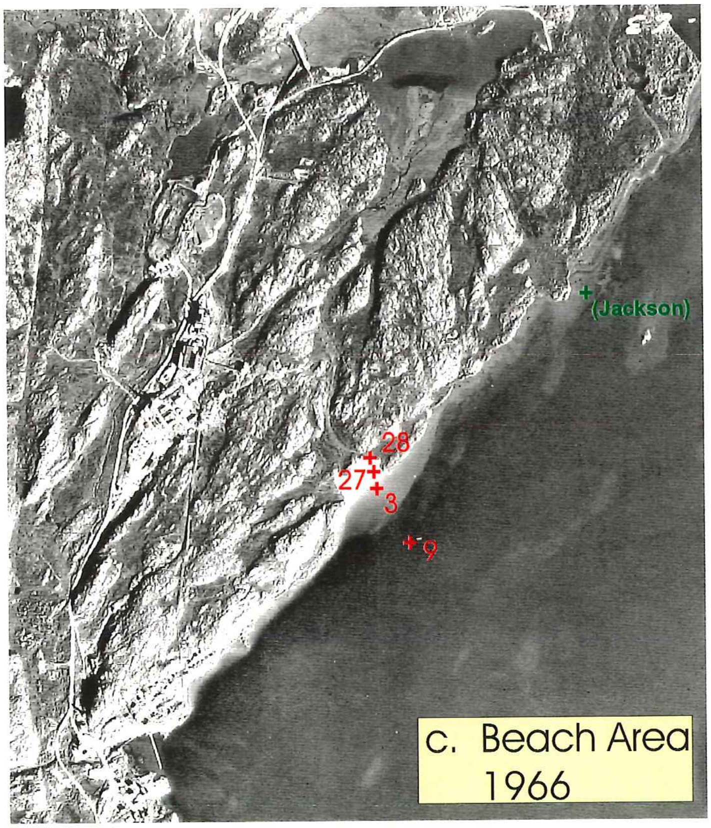


Photo VI-1: Beach Tailings Area (a)1945 (b) 1950



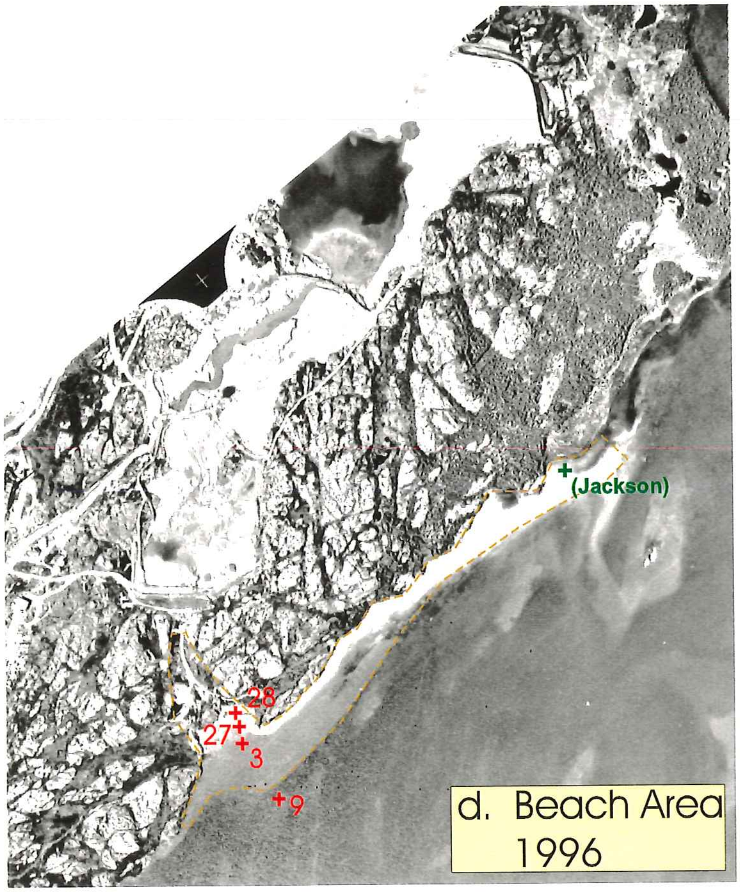


Photo VI-2: Beach Tailings Area (c) 1966 (d) 1996

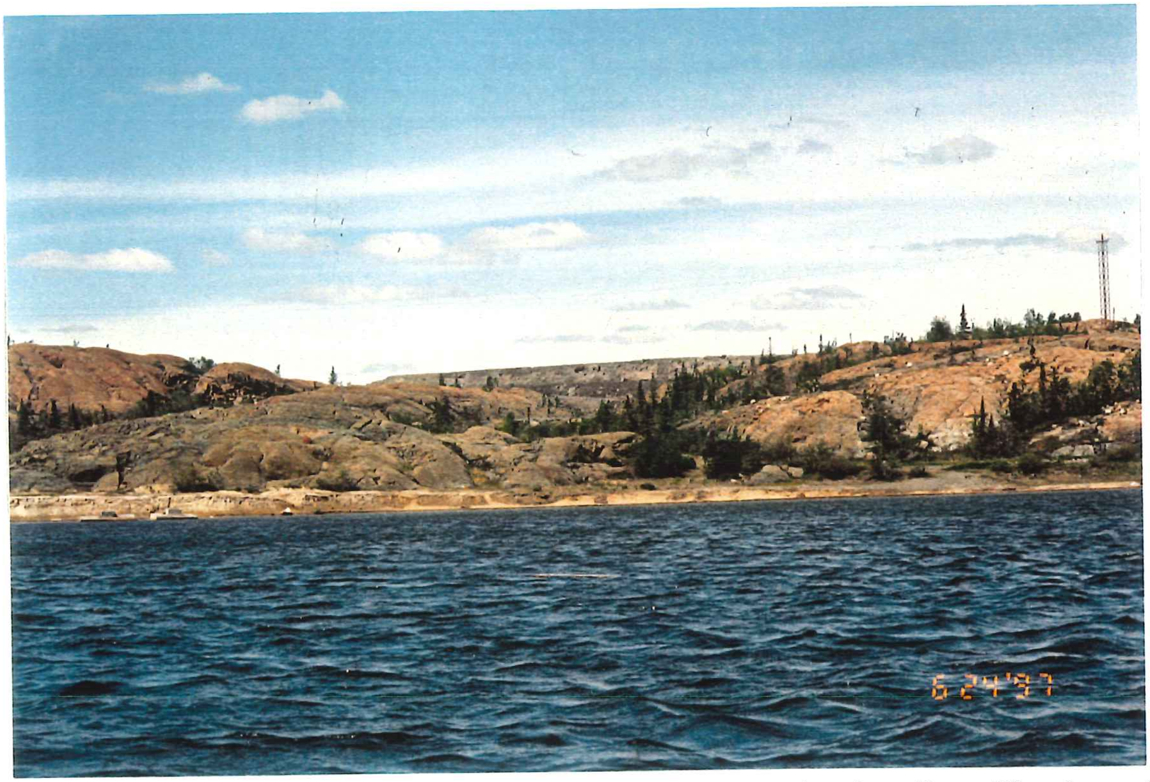

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Photo VI-3: Beach Area showing tailings build-up along the shoreline. The dam of the South Pond is visible in the background.

The depth of the tailings covering this area cannot be accurately estimated at this time. On shore, the tailings are approximately 2 m above the water level with erosion ongoing (Photo VI-3). At sample location #27, a 20 cm core was obtained without reaching the bottom of the tailings (Photo VI-4) as confirmed by visual inspection and the second PCA (Figure VI-4). At sample location #3, the density of the tailings were not conducive to the collection of a deep core. A core of only 7 cm in depth was collected.

The depth of the tailings within the small bay and throughout the entire area affected by the erosion of the tailings is unknown. An estimated depth of 20 cm was assumed over the entire area of tailings in the water for the load calculations. It is assumed that the depth of tailings diminishes as the distance from the Beach increases. Therefore, 20 cm is a conservative estimate for the depth of the entire Beach Tailings Area.

As noted above, the Beach Tailings Area is estimated to directly cover an area of at least 16 ha. Assuming an average depth of 20 cm throughout this area, the Beach Area consists of roughly 33 000 m^3 of tailings within Yellowknife Bay. The average

concentration of these tailings is 910 ppm arsenic. The Beach Tailings Area estimated to contain 44 tonnes of arsenic at a determined density of 1500 kg/m^3. This volume of tailings and mass of arsenic does not take into account the tailings on shore between the water and the South Pond.

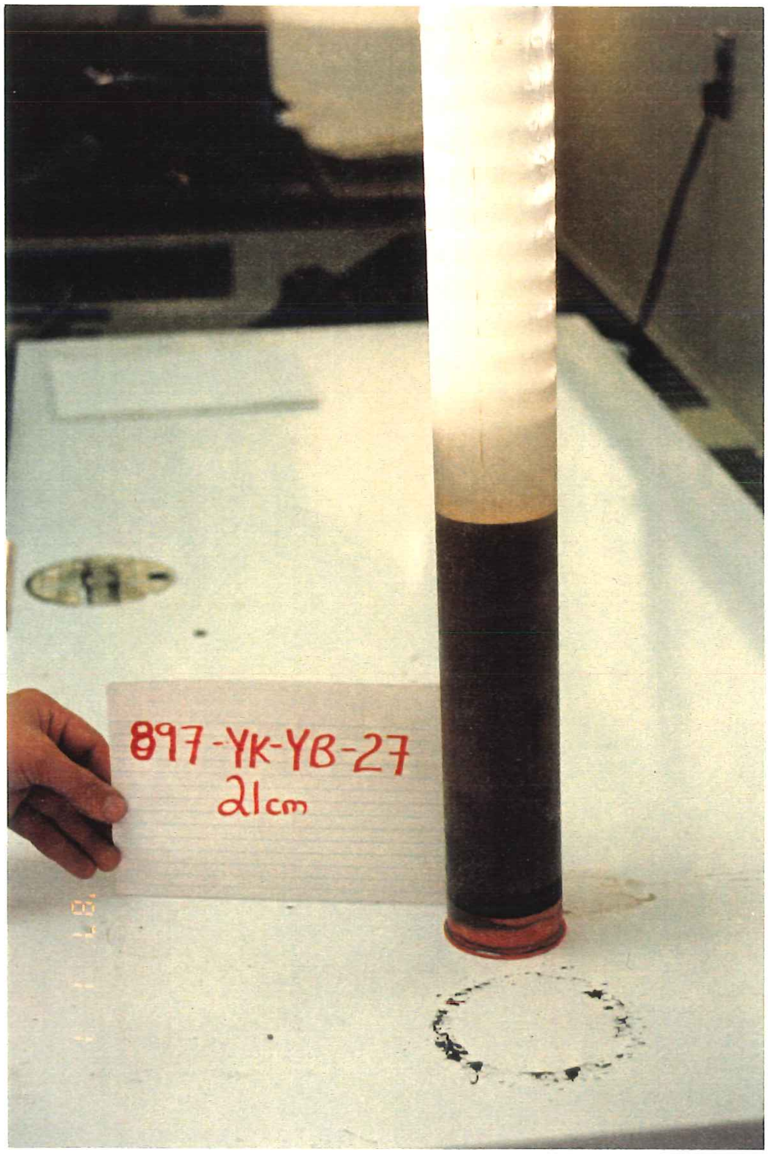


Photo VI-4: Sediment core obtained at sample location #27 within the Beach Area.

The Beach Tailings Area also consists of tailings deposited in the small valley that runs from the bay to the southern dam of the South Pond. This area is known to consist of tailings (Schultz, 1998). Over the years, vegetation has grown over certain sections. It is impossible to even estimate the depth and/or volume of these tailings at present as a thorough investigation of this area has not been conducted.

3. Baker Creek

Many of the samples obtained throughout Baker Creek contain elevated arsenic levels (XRF analysis) down to a depth of 15 cm (Table VI-6). The surface values are from sediment samples obtained with plastic scoops and placed in Whirlpack^{TM} bags.

The order of the samples in Table VI-6 runs from upstream of the effluent (#24 and #29) to the Baker Creek outlet (#22). It is apparent that the upper layer of sediment from the effluent discharge area (#20) to the outlet area contains high arsenic levels. These levels would appear to be maintained within the top 10 cm of sediment, with a definite decrease occurring at 10-15 cm in depth.

Table VI-6: Arsenic levels (ppm) found at depth in the sediments of Baker Creek

Depth (cm)	**24**	**29**	**BC-30**	**20**	**19**	**18**	
0-5	41	114	238	2332	3707	4227	
5-10				2225		793	
10-15				309			
	17(June)	**17(Aug.)**	**16**	**10**	**22**	**Average**	**Arsenic Load (kg)**
0-5	2150	7460	1914	278	2197	2880	7120
5-10	4521	6397			1713	1580	3930
10-15		5914			206	260	640
						Total	**11 700 kg**

The arsenic concentrations at sample location #17 appear to be inconsistent with the concentrations found at the other sample locations. Not only does it have the highest concentration of any location within the creek, but also the arsenic concentration does not begin to decrease at 5 or 10 cm to the same degree as the other sample locations (Table VI-6). Due to this marked difference, the arsenic concentrations at sample location #17 were not used for the estimation of the average arsenic concentrations throughout the creek at the various depths.

The arsenic load was determined for the top 15 cm of sediment for the section of Baker Creek between sample locations #20 and #22 (Table VI-6). This area was estimated to be 62 ha in area with a volume of 9300 m^3 for the top 15 cm of sediment. The average dry sediment density was determined to be 790 kg/m^3. The average concentration of arsenic at each 5 cm increment was used with the surface samples being included in the 0-5 cm grouping. Sample location #24 was not included in the loading calculation because of its background concentration of arsenic. Sample locations #29 and #BC-30 were not included as they did not come under direct influence of the mine effluent discharge and have relatively low arsenic concentrations.

4. Yellowknife Bay

The highest concentrations of arsenic and the area of main concern is the Baker Creek outlet area within the Bay. Sample locations #4 and #21 were collected in this area and arsenic concentrations were determined down core. For comparison, the values obtained at depth from two previous reports with sample locations near sample location #21 were included (Table VI-7).

Table VI-7: Arsenic concentrations (ppm) found at depths in the sediments of Yellowknife Bay

Depth (cm)	**9**	**4**	**21**	**Sutherland (1989)**	**Mudroch *et al.* (1989)**	**25**
0-5	525	3623	1428	1868	997	509
5-10	454	10710	610	967	165	173
10-15	1057		260	200		116
15-20	395			110		130
20-25	148					

Sample location #4 exhibits the highest arsenic concentrations within Yellowknife Bay due to its close proximity to the outlet. The deposition of particulate matter with elevated arsenic concentrations coming from the creek is likely the major source followed by the adsorption/co-precipitation of dissolved arsenic with iron and manganese oxides.

Farther out in the Bay, sample location #21 and the samples from the two previous reports (Mudroch *et al.*, 1989; Sutherland, 1989) contain similar arsenic concentrations. At a depth of 10 cm, there is a drop off in the concentration of the arsenic.

Estimating the area containing these high levels or the load of arsenic within this area is difficult given the current information. It is estimated that the heavily contaminated area measures 1000 m directly out from the outlet and 800 m wide giving an area of 800 ha.

For load estimations within this area, average estimated arsenic concentrations are taken as 1500 ppm, 1000 ppm and 200 ppm through the top 15 cm. These values are once again conservative estimates based on the assumption that the area of highest arsenic concentration is found near sample location #4. It is expected that the concentration of arsenic out from location #4 will decrease. The dry weight density of the sediments was determined to be approximately 470 kg/m^3 with a volume of 120 000 m^3 for the top 15 cm of sediment. Using these estimates, there is approximately 51 tonnes of arsenic within Yellowknife Bay outside of the Baker Creek outlet.

As previously discussed, sample location #9 is close to the estimated extent of the beach tailings. The depth profile for arsenic shows that more than just the surface sediments have been affected by arsenic redistribution from the Beach Tailings.

5. *Total Arsenic Load*

The load calculations are summarized in Table VI-8. Upon first examination, the estimated 107 tonnes of arsenic found within the Beach Tailings, Baker Creek and Yellowknife Bay appears relatively insignificant in comparison to the arsenic found on mine property (i.e. baghouse dust and tailings ponds). However, arsenic found directly within the aquatic environment has a greater probability of immediate detrimental effects.

Table VI-8: Summary of arsenic load calculations

Area	Area (ha)	Volume (m^3)	Average Arsenic Concentration (ppm)	Arsenic Load (tonnes)
Baghouse Dust				≈200 000 *
Tailings Ponds	116	13 000 000	2700	41 400
Beach Tailings	16	33 000	910	44
Baker Creek	62	9300	1500	12
Yellowknife Bay	800	120 000	900	51

*tonnes of arsenic trioxide found within the mine shafts (Royal Oaks, 1997)

D. Porewater

1. *Porewater Analysis*

Arsenic is not necessarily permanently removed from the aquatic environment upon precipitating with or sorbing onto the sediment phases. The cycling of arsenic within the porewater is affected by redox conditions, iron and manganese oxides, and the presence of sulphides (II.E). The arsenic, iron and manganese concentration profiles of the porewater and sediments were determined at a number of sample locations in order to investigate the potential for arsenic to remobilize from the sediment (Table VI-9). The locations chosen cover the area affected by the effluent discharge (#20, #22, #4 and #21) and three locations within Yellowknife Bay (#2, #9 and #25) with all cores being taken in June. Figure VI-6 displays the down core profiles for arsenic, manganese and iron in the porewater and sediment for sample locations #9, #20, #21 and #25; tabulated values are presented in Table VI-9. These four sample locations were chosen as they are representative of the seven analyzed cores.

Table VI-9: Porewater profiles of various cores

Sample	**Depth**	**Porewater[a]**			**Sediment[b]**		
	(cm)	**As (ppb)**	**Mn (ppm)**	**Fe (ppm)**	**As (ppm)**	**Mn (ppm)**	**Fe (ppm)**
20	0-5	1336	0.04	0.84	2332	168	16490
	5-10	504	0.42	1.05	2225	172	16113
	10-15	755	0.59	8.18	309	208	10700
22	0-5	1384	2.31	25.63	2197	412	35448
	5-10	1491	0.16	4.76	1713	450	33370
	10-15	1760	3.13	21.25	206	348	28903
4	0-5	1642	0.57	0.70	3726	424	20717
	5-10	3371	0.80	0.65	10710	691	25011
21	0-5	794	1.61	2.80	1428	1610	41982
	5-10	1708	8.75	26.60	610	819	38726
	10-15	1919	8.35	26.65	260	1102	36332
2	0-5	22	0.72	4.34	Not analyzed		
	5-10	76	0.44	6.63			
	10-15	33	0.20	1.05			
9	0-5	57	0.75	1.00	525	482	33018
	5-10	158	0.85	0.60	454	304	27685
	10-15	207	1.49	11.60	1057	327	35633
	15-20	145	0.98	1.90	395	399	30770
25	0-5	188	1.90	7.20	509	1057	40490
	5-10	307	1.90	8.60	173	445	34340
	10-15	195	2.94	20.29	116	460	35930

[a] Dissolved phase concentrations of indicated elements.

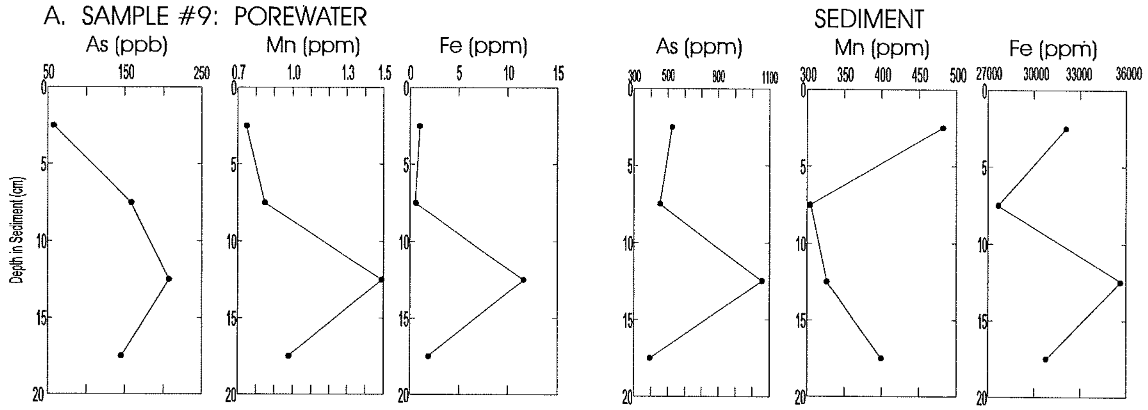
[b] Solid phase concentration of indicated elements.

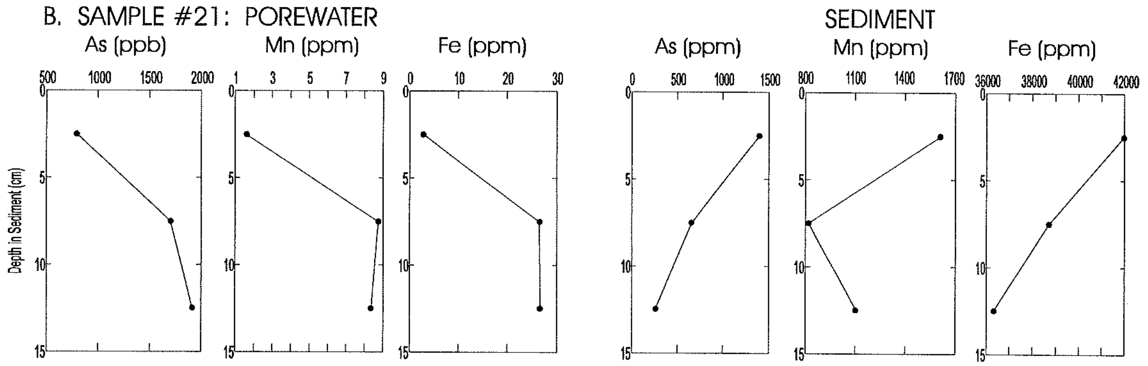
The sample locations affected directly by the effluent discharge (#4, #20, #21 and #22) have higher arsenic concentrations within the sediments and porewater than do the other locations within Yellowknife Bay (#2, #9 and #25). A comparison with the summary of known biological effects for arsenic in surface water (Figure II-1) suggests the potential for detrimental effects on organisms within the benthic community. Concentrations of As(V) ranging from 48 to 690 ppb have been shown to cause reduced growth in various algae. Detrimental effects on freshwater invertebrate have been observed from 88 ppb (As(III)) to 850 ppb (As(V)) (Eisler, 1994). The uptake of arsenic by benthic organisms is thought to be related to the concentration of arsenic in the surface porewater (Cullen and Reimer, 1989). The elevated concentrations of arsenic in the porewater (up to a maximum of 3371 ppb at sample location #4) indicate that there is a significant potential for arsenic redistribution from sediments to benthic biota.

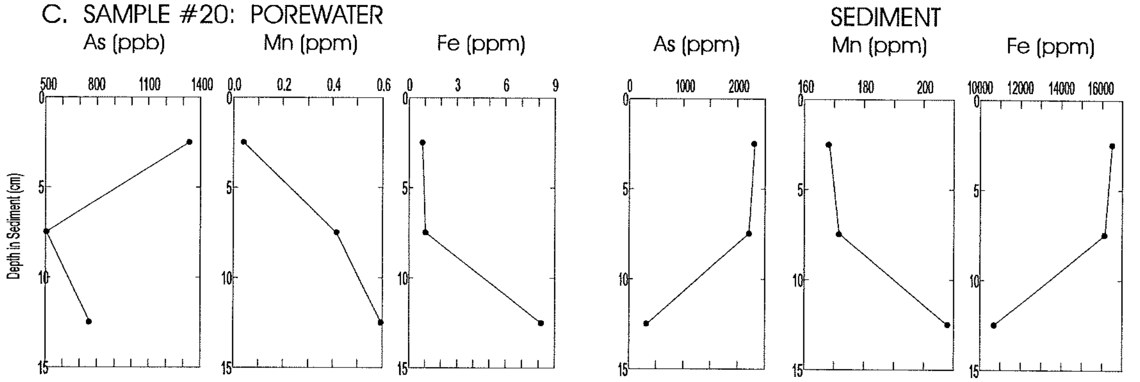
The observed dissolved arsenic maxima is more closely related to the maximum concentrations of dissolved iron and manganese than to the arsenic concentrations in the surficial sediments. At sample locations #2, #9, #21 and #25, the maximum concentrations of dissolved arsenic and iron occurred at the same level. This corresponds to the findings in the study by Peterson and Carpenter (1986) and indicates that the dissolution of arsenic into the porewater is closely related to the dissolution of iron oxides. The maximum dissolved iron (Fe^{2+}) peak at a depth of 10-15 cm is likely due to the reduction of the iron oxides by burial of the sediments and seasonal variations of the redox transition level (Belzile and Tessier, 1990).

The porewater concentration profiles for manganese and iron demonstrate that the porewater maximas occur at similar depths (Figure VI-6). The maximum for both iron and manganese was found in the 10-15 cm section with the concentration of manganese generally being an order of magnitude less. It was stated that the release of arsenic by the dissolution of manganese is often counteracted by the re-adsorption onto iron oxides. There is insufficient information to state whether this occurs at these sample locations.

Sufficient core depth was not obtained at sample location #4 to use it in comparison with the other locations. However, the arsenic concentrations of 3371 ppb in the porewater and the 9420 ppm in the solid phase at 5-10 cm were the highest concentrations found.


A. SAMPLE #9: POREWATER SEDIMENT


B. SAMPLE #21: POREWATER SEDIMENT


C. SAMPLE #20: POREWATER SEDIMENT

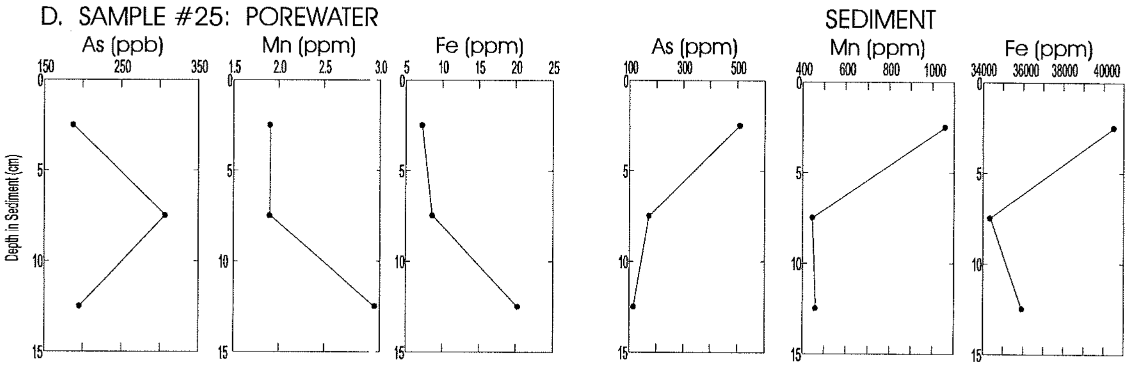

D. SAMPLE #25: POREWATER SEDIMENT

Figure VI-6: Sedimentary porewater and solid phase elemental concentrations for samples, #9, #20, #21 and #25 in Yellowknife Bay.

The maximum dissolved arsenic concentration at sample location #20 occurred in the 0-5 cm section with the maximum Fe^{2+} at 10-15 cm. However, the dissolved arsenic concentration increases from the 5-10 cm section to the 10-15 cm section as predicted. The location of the dissolved arsenic maxima could be due to the proximity of the effluent discharge and would appear to not reflect a steady-state situation.

The maximum concentrations of arsenic and iron in the sediments occur in the top section of the cores from sample locations #20, #21, #22 and #25. The location of the dissolved arsenic maxima below that of the surface sediments indicates that the upward diffusion of dissolved arsenic followed by adsorption and/or co-precipitation with iron oxides may be a source for the surface sediments (Peterson and Carpenter, 1986). This upward diffusion is likely secondary to the continuous sorption and co-precipitation of arsenic with iron oxides within the water column followed by deposition derived from the anthropogenic discharge of arsenic.

In general, the concentration of arsenic, iron and manganese in the solid sediments decreases with depth. Conversely, within porewater, the opposite holds true. This coincides with the cycling diagram (Figure II-3). At greater depths in the sediments, the redox conditions will be conducive to the dissolution of arsenic, iron and manganese. Once in the dissolved phase, these will move upwards and the dissolved iron and manganese will precipitate upon reaching the oxic zone followed by the adsorption/co-precipitation of arsenic. The higher levels of arsenic, iron and manganese in sediment near the sediment/water interface is possibly due to a combination of this cycling and the adsorption/co-precipitation of arsenic with iron and manganese oxides from the water column.

2. *Arsenic Flux*

It is of importance to determine if the upwards flux of arsenic within the sediments provides a mechanism by which arsenic can be mobilized into the overlying water column.

a) Method of Calculation

The calculation of the arsenic flux from the sediments to the water column was carried out using the method outlined by Azcue and Nriagu (1994). This method is based on Fick's first law, which calculates the diffusive flux. It does not take into account of the movement of the porewater due to the hydraulic gradient.

$$F = \phi\, Ds\, (dC/dZ)_{x,y}$$

Where - F is the diffusive flux of As ($\mu g\ cm^{-2}\ y^{-1}$)

- ϕ is the average porosity of the sediments from surficial sediments to the depth of the maximum porewater concentration of arsenic
- Ds is the diffusion coefficient in porewater ($cm^2\ y^{-1}$)
- $(dC/dZ)_{x,y}$ is the arsenic concentration gradient which is represented by $\Delta As/\Delta z$ due to the linearity of arsenic concentrations. ΔAs is the concentration difference between bottom water and porewater at the depth of the concentration maximum, Δz.

For this calculation, various assumptions are made:

- the sediment/water interface is known
- viscosity and charge coupling effects are negligible
- arsenite and arsenate are the only forms of As present and have the same diffusion properties
- the solid phase, at the sediment/water interface, does not absorb dissolved As
- arsenic concentrations are linear throughout the porewater

For the calculation of the diffusion coefficient, the equation $Ds = \phi^2 D$ is used where D is the diffusion coefficient of the arsenic ion at infinite dilution, is 5.3×10^{-6} $cm^2 s^{-1}$ (Peterson and Carpenter, 1986; Reimer and Thompson, 1988; Azcue and Nriagu, 1994).

Porosity is the ratio of the volume of voids to the total volume of soil (Craig, 1987) with volume of voids being the volume of porewater found within a section of sediments. The porosity of the sediments was not obtained from core samples because they were all squeezed to remove the porewater. Therefore, an average porosity from surficial sediments to the depth of the maximum porewater concentration of arsenic was not obtained. The porosity values were determined using the sediment grab samples obtained at sample locations #21 and #25, which were frozen immediately after collection. Small sections of the frozen samples were chipped off and placed in graduated cylinders with known volumes of water. This allowed for the determination of the total volume of sediment. The cylinder was placed in an oven overnight to obtain the dry mass, which was compared to the total wet mass to determine the volume of voids. Porosity values of 0.71 and 0.79 were determined for sample locations #21 and #25. The value of 0.71 was used for the other sample locations because no sediment grabs were collected from these locations.

Mudroch (1989) quoted surface porosity values of 0.88 and 0.91 near sample locations #21 and #25, respectively. Peterson and Carpenter (1986) determined porosity values ranging from 0.70 to 0.95 in marine sediments. Reimer and Thompson (1989) used an estimated average porosity of 0.8 for natural marine sediments.

A loss of water during the collection of the sediment grabs could explain the lower determined porosity values in this study in comparison to those determined by Mudroch (1989). These porosity values do not take into account the change in porosity which occurs at depth due to compression of sediments. A core should be collected for the sole purpose of determining the average porosity of sediments with the average porosity being determined immediately.

b) Factors Affecting the Flux

No method of flux calculation is without sources of error. There are a number of factors which can have an effect on the flux that are not taken into account within Fick's first law. The assumption that the arsenic concentrations are linear may not hold true due to the heterogeneous composition of sediments near the sediment/water interface (Santschi *et al.*, 1990). Ficks's law is based upon molecular diffusion, which underestimates arsenic flux (Millward *et al.*, 1997).

Various factors within the environment can have a direct influence on the flux. In a controlled study, it was shown that the burrowing of benthic invertebrates can lead to an increased flux of arsenic. It is also possible that these organisms can further transmit contaminants by intake of the contaminants followed by predation (Riedel *et al.*, 1989). The flux of arsenic from the sediments was shown to increase at high or low pH levels (Mok and Chien, 1990). Another controlled study investigated the effect of oxygen conditions on the flux. In anoxic conditions, a substantial arsenic flux was observed in comparison to the flux in oxic conditions. This difference was said to be due to the precipitation of Mn and Fe hydroxides at the surface with the arsenic being adsorbed/co-precipitated (Riedel *et al.*, 1997). It is likely that the actual flux of arsenic will vary throughout the year as the oxygen levels within the water column fluctuate.

c) Results Obtained

The arsenic fluxes and accumulation rates were calculated for five sample locations throughout Yellowknife Bay (Table VI-10) with the samples collected in June. The calculated flux values are representative of the maximum possible fluxes of arsenic from sediments into the water column (Peterson and Carpenter, 1986) assuming that adsorption/co-precipitation does not occur within the oxidized surface layer (Reimer and Thompson, 1988). For the calculation of the accumulation of arsenic, the sedimentation rate of 0.37 cm y^{-1} was used for sample location #25 and 0.24 cm y^{-1} for the remaining sample locations (Mudroch *et al.*, 1989). Flux calculations for the Beach samples (#3 and #27) could not be completed due to the small grain size of the tailings, which did not allow for the collection of porewater samples.

Table VI-10: Calculated arsenic flux and accumulation values

Sample	Porewater Depth (cm)	As in Porewater (ppb)	As in water column (ppb)	Diffusive Flux (μg cm^{-2} y^{-1})
4	0-5	1642	2.4	
	5-10	3371		26.9
8	0-5	38	23.7	
	5-10	74		
	10-15	148		0.6
	15-20	45		
9	0-5	58	1.3	
	5-10	159		
	10-15	207		1.0
	15-20	146		
21	0-5	794	0.9	
	5-10	1709		
	10-15	1920		9.2
25	0-5	188	11.4	
	5-10	306		3.2
	10-15	196		

For both sample locations #4 and #21, the calculated fluxes may be overestimated since it is not known if the actual porewater maximum was determined as a reduction in arsenic porewater concentration was not observed at the depths obtained. Deeper cores are required to ensure that the correct porewater maximums are used. These two locations have the greatest flux and rate of accumulation since they are situated in the Baker Creek outlet area and have the highest arsenic concentrations in the porewater and sediments. The elevated levels of arsenic due to pollution promote the upward diffusion by increasing the gradient between the porewater and the water column (Cullen and Reimer, 1989). The results of Table VI-10 strongly suggest that arsenic can be mobilized from contaminated sediment in Yellowknife Bay. The upward movement of arsenic will not necessarily be stopped if these sediments are covered by uncontaminated sediments once mining operations have ceased.

Azcue *et al.* (1994) investigated the arsenic flux for the sediments of Moira Lake, Ontario, which were contaminated by past mining activities. The average arsenic concentration of the sediments was found to be 545 ppm with values up to 1000 ppm. The average arsenic concentration of the surface water in the summer was determined to be 47 ppb. The calculated diffusive fluxes ranged from 0.77 to 3.85 μg cm^{-2} y^{-1}. Peterson and Carpenter (1986) determine fluxes in the marine environment along the western coast of Washington State and British Columbia ranging from 0.37 to 2.4 μg cm^{-2} y^{-1} for sediments with arsenic concentrations ranging from 7 to 37 ppm. The upwards fluxes calculated in this study at sample locations #4 and #21 exceed what was reported in the other studies due to the high levels of arsenic at these locations.

The upward movement of dissolved arsenic in porewaters is primarily controlled by diffusion (Cullen and Reimer, 1989) with benthic organisms (Riedel *et al.*, 1989) and the upward movement of porewater due to sediment compaction (Cullen and Reimer, 1989) playing a minor role. A thin oxic layer, due to a high sedimentation rate of easily metabolized organic matter, may not be able to stop all of the arsenic from diffusing upwards into the water column (Cullen and Reimer, 1989).

E. Arsenic Forms

A sequential extraction test and leachate tests were performed on various samples in order to ascertain the major phases with which the arsenic was associated and the potential for dissolution into water. These factors can influence the bioavailability and potential input of arsenic in the study area.

1. Sequential Extraction

A sequential extraction test can be used to determine the particle speciation of metals within the environment. This aids in the determination of the source of arsenic and the stability of the arsenic within the sediments and tailings. The method used was set out by Tessier *et al.* (1979) and consists five fractions, as previously described.

a) Benefits of Sequential Extraction

Most studies use total concentration of an element as their basis of comparison to determine the potential effects of contaminated sediments. This is based on the assumption that all forms of the element in question have equivalent availability to the environment, which is untrue. On the other hand, the sequential extraction tests can provide information on the origin, mode of occurrence, bioavailability, mobilization, and transport of trace metals (Tessier *et al.*, 1979)

b) Limitations of Sequential Extraction

Sequential extraction methods are generally considered to be operationally defined. This means that the results obtained are defined by the extractants used, i.e. the acetate buffer will extract the "acetate-buffer-extractable" phase (Kheboian and Bauer, 1987).

Kheboian and Bauer (1987) evaluated the accuracy of the Tessier method. The two main sources of error derived from sequential extraction are the likelihood of the dissolved metals to be redistributed to other phases and the non-selectivity of the extractants used. Other potential problems are as follows:

- There is no standard with known element phase distribution that can be used to verify results.
- The water wash between methods leads to a loss of some dissolved metals
- The extraction of the bound to organic matter phase is very violent and can result in the loss of some material from the containers
- Effective duplication of results does not necessarily indicate an accurate extraction scheme.

c) Results Obtained

Even with certain obvious areas of inaccuracy, sequential extraction can still aid in the identification of trends and the availability of a specific metal. A sequential extraction using Tessier's scheme was conducted on 15 sediment and tailings sample locations chosen to cover the sediments heavily affected by the effluent discharge. The results obtained are presented as the percentage of the total arsenic within each of the 5 phases (Figure VI-7) and the amounts of arsenic within each phase (Table VI-11).

The amount of arsenic within the organic phase was not determined due to the loss of sample during the extraction step for sample locations #36 and #45. It is readily apparent that, with few exceptions, there is a difference in the partitioning of arsenic within the sediment samples and the tailings. The dominant portion for the sediments was the arsenic bound to Fe and Mn oxides, whereas in the tailings, arsenic was mainly associated with the residual phase.

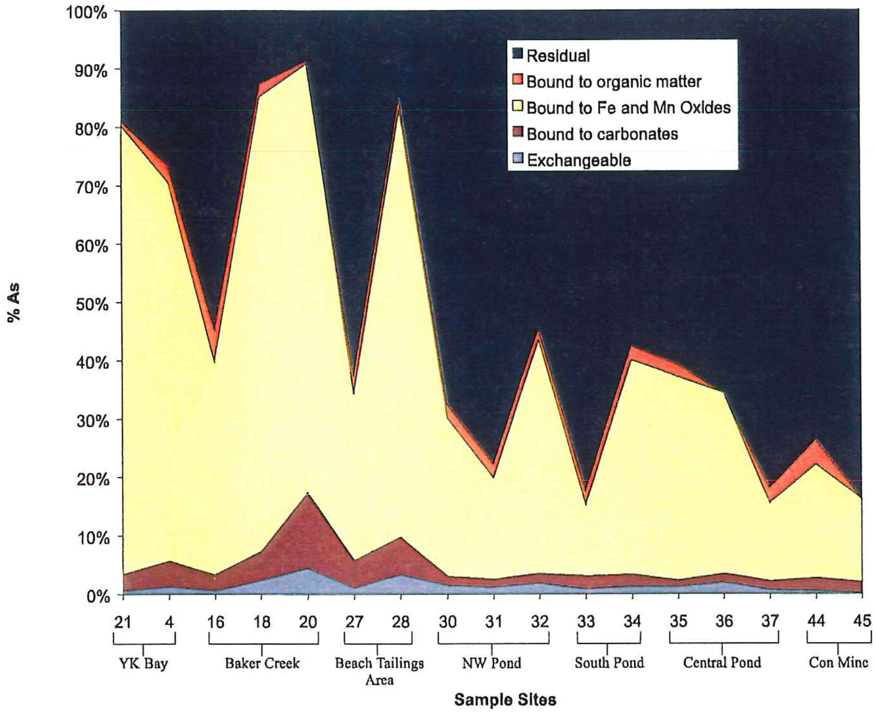


Figure VI-7: Sequential extraction of tailings and sediment samples (% of total As).

This finding corresponds with the study by Azcue and Nriagu (1993), which consisted of a sequential extraction test on mine-polluted sediments from Moira Lake, Ontario. Overall, 56% of the arsenic was found to be associated with the Fe and Mn oxides. They predicted that in areas not affected by pollution, the order of the phases would be residual > organic/sulphide > Fe and Mn oxide > exchangeable > carbonate. However, in areas of increased arsenic input, a larger amount of arsenic becomes bound to Fe and Mn oxides. The resulting predominance was found to be Fe and Mn oxide > residual > organic/sulphide > exchangeable > carbonate. This was believed to show that the arsenic from the mine waste was still controlling the cycling of arsenic in the area.

Moore *et al.* (1988) obtained similar results with sediments from a contaminated river in Montana. For sediments in the oxidized zone, the dominant fraction was found within the Fe and Mn oxides. However, it was determined that in the reduced zone, the sulfide fraction was dominant. This corresponds with the fact that in anoxic conditions, trace elements can be co-precipitated with, or sorbed onto iron sulfides.

Table VI-11: Arsenic levels (ppm) found in each of the 5 phases

Sample Location	Exchangeable	Bound to Carbonates	Bound to Fe and Mn Oxides	Bound to Organic Matter	Residual	Total Arsenic
21	7	33	917	9	226	1193
4	41	137	2039	92	830	3140
16	11	49	658	98	948	1764
18	68	139	2211	61	358	2838
20	78	223	1275	9	150	1736
27	8	35	211	22	463	738
28	33	62	712	20	148	974
30	53	54	944	83	2360	3494
31	57	64	841	115	3765	4842
32	60	54	1286	60	1611	3072
33	15	39	210	42	1433	1738
34	38	57	1030	68	1614	2807
35	36	28	954	58	1664	2740
36	55	40	844	0	1791	2730
37	24	49	439	85	2703	3301
44	11	40	372	81	1414	1919
45	4	30	233	0	1376	1643

The dominant phase found within the sediments of Baker Creek and Yellowknife Bay is the bound to iron and manganese oxides. This indicates that the arsenic in the effluent discharge, which is the dominant source of arsenic, is in the dissolved form. Upon reaching the creek, the arsenic undergoes sorption onto and/or co-precipitation with the iron and manganese oxides. The potential exists for the redistribution of the arsenic into the water column during anoxic conditions, due to the large bound to iron and manganese oxide phases within the sediments.

This will likely not occur within the sediments of Baker Creek as it is unlikely that the surface sediments and water column will become anoxic due to the flow of water. However, this does not preclude bulk transport of creek sediments. Periods of anoxic conditions within the water column of Yellowknife Bay may occur in late summer and during the winter. These conditions would be conducive to the reduction and dissolution of the iron and manganese oxides thereby releasing the adsorbed arsenic. It is important to conduct under-ice sampling to determine the likelihood of this scenario.

The tailings pond samples vary greatly from the sediment samples with the residual phase being dominant. Sample location #28 differs greatly from the other tailings samples. It was collected from a dried water runoff area 10 m from the shore of Yellowknife Bay in the Beach Area. According to the surface sample PCA (Figure VI-3), it has similar characteristics to the other beach samples. It is unknown why it had such a large fraction of arsenic bound to Mn and Fe oxide phase in comparison to the other tailings samples.

The fact that the tailings have larger residual fractions corresponds with the Giant Mine's belief that the arsenic found within the tailings is found in a more stable form, possibly ferric arsenate, due to the treatment process (Royal Oak, 1997). There is also a definite similarity between the tailings from the Con Mine and those from the Giant Mine. Even with the majority of the arsenic in the tailings samples in the residual fraction, there still exists a large amount of arsenic within the four more bioavailable phases. In the Giant Mine samples (#30 to #39), the average total arsenic concentration of these other fractions is about 1000 ppm.

2. *Leachate Test*

To further investigate the availability of the arsenic in the sediments and tailings near the Giant Mine, leachate tests were conducted on a range of samples. The test procedure was based on the method found in Regulation 347: General-Waste

Management Regulation of the MOEE (MOEE, 1990). The leachate quality criteria for arsenic is set at 50 ppb. However, a substance is considered to be "leachate toxic waste" when the concentration of a given element exceeds the criteria by two orders of magnitude. Therefore, for a sample to be considered leachate toxic waste, the leachate concentration must exceed 5000 ppb.

Leachate tests were conducted on 15 different samples (Figure VI-8) chosen with the importance placed on the tailings samples to determine the leachability of the arsenic within the tailings ponds. Three sediment sample locations were chosen to provide a comparison with the sequential extraction results. The sequential extraction test was conducted on all of these samples, except sample locations #3 & #39. Only sample location #20 would be considered leachate toxic waste. While not exceeding the toxic standard, two thirds of the sample locations exceeded the 50 ppb drinking water criteria demonstrating that arsenic can leach from these materials.

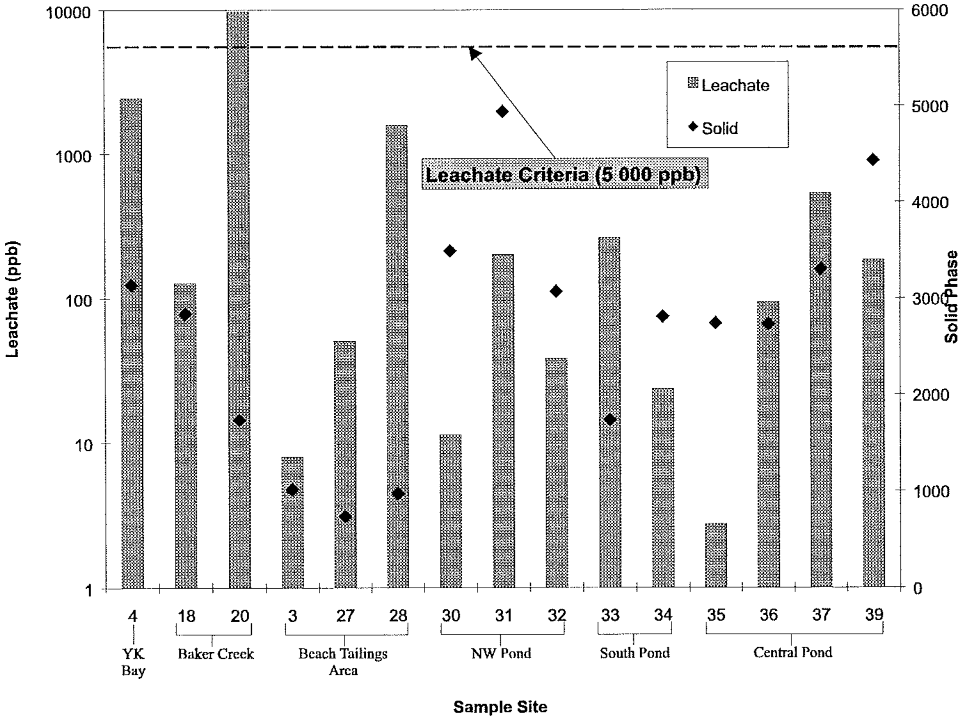


Figure VI-8: Arsenic leachate results

Distinct similarities are seen between the results obtained by the leachate tests and the sequential extraction tests. The majority of the arsenic in the sediment samples (#4, #18 and #20) was found within the more bioavailable Fe and Mn oxides phase. The majority was found within the residual phase for the tailings samples. The average leachate concentration is 4100 ppb for the sediments and 130 ppb for the tailings (excluding #28). This difference is not attributable to higher arsenic concentrations within the sediment. The average arsenic concentration within the tailings exceeds that of the sediments by 300 ppm. This further confirms that the arsenic within the tailings ponds is in a relatively stable form.

It is apparent that the arsenic within the sediment is more available to the environment than the arsenic in the tailings. The majority of the arsenic in the sediments is bound to the Mn and Fe oxide phase. This phase is more available to the environment as shown by the leachate test. This was further confirmed by the high levels of arsenic found within the porewater of contaminated sediment locations (Table VI-9).

Sample location #28 once again appears to be an anomaly. Even with its relatively low arsenic concentration, it had the third highest concentration of arsenic within the leachate. This can be linked directly to the previous findings of a large arsenic phase bound to the iron and manganese oxides.

VII. POSSIBLE REMEDIAL SOLUTIONS

This study clearly demonstrated that the mine has been responsible for the input of considerable amounts of arsenic into the environment. It was, however, beyond the scope of this project to evaluate whether the contaminants are having a negative impact on the local environment. It is, however, instructive to consider the available options should reclamation be required. Accordingly, several options were evaluated and estimates made of the associated costs, which include labour.

A. Tailing Ponds

The sequential extraction and leachate tests demonstrated that the arsenic within the tailings, while more stable than the arsenic in the sediments, can possibly leach into the environment. This could occur by surface water runoff or water seepage into the groundwater. Further dispersion of the tailings could occur from wind erosion and redistribution of particulates.

1. Areas of Concern

The need for reduction of groundwater contamination has not been sufficiently addressed. Results obtained by the Giant Mine (Royal Oaks, 1997) show that there is little groundwater flow within the southern portion of the South Pond. However, this conclusion cannot be applied to all of the tailings ponds. As can be seen in the progression of the aerial photographs (Photo VI-1 & Photo VI-2), portions of the North, Central and South Pond are located where a lake was once present. It is possible that the groundwater is flowing through the lower sections of the tailings and being contaminated. Even if this is not the case, surface water may be seeping through the tailings dams and down into the groundwater table. However, there is currently insufficient information to determine whether contamination of the groundwater is, or will be, a problem.

Wind erosion of the tailings is a definite possibility considering the semi-arid climate in Yellowknife. At the time of sampling in August 1997, the surface tailings of the Central and South Ponds were dry. Once mining operations have ceased, the same situation would likely occur with the remaining tailings. This situation is conducive to wind transport.

Surface water runoff can lead to the leaching of arsenic and the erosion of the tailings. This would most likely occur during the spring thaw. Both of these further forms of contamination are possible with improper longtime maintenance of the tailing ponds. They could result from the failure of the various dams with the subsequent bulk displacement of tailings and/or leaching of more arsenic into the local environment.

2. *Possible Solutions*

a) Geosynthetic Solution

The use of geosynthetics to cap the tailings ponds has the capability of almost completely stopping any exposure of the tailings to surface water and wind erosion. This approach would control the generation and subsequent migration of metal leachate (MNDM, 1994) and the downward flow of surface water into the groundwater table. However, it would not eliminate the potential for groundwater contamination if the groundwater flows through the lower portions of the tailings. A detailed groundwater survey of the area is required to determine if capping would be effective in reducing groundwater contamination. A geomembrane may also result in reducing conditions within the tailings pond and an increase in released arsenic from the tailings.

The US EPA has a recommended landfill cover design for closed hazardous waste management units. The design consists of, from bottom to top, a low permeability layer, a drainage layer (30cm), a filter layer and a vegetation/soil top layer (60 cm). The low permeability layer consists of a 0.5 mm geomembrane layer underlain by a 60 cm layer of compacted natural or amended soil (Landreth and Carson, 1991). For areas where finding aggregate and low permeability soil is difficult, the 30 cm drainage layer and 60 cm layer of compacted soil can be replaced by a geocomposite/geonet drain and a geosynthetic clay liner (Koerner, 1994). It should be noted that the US EPA recommendations are not site specific. They are designed to work in all conditions, which can lead to the possibility of over engineering.

The costs of using a geomembrane for capping the tailings ponds was investigated. Nilex Inc. (Kehler, 1998) quoted prices for budget purposes of three possible materials: 1) high density polyethylene (HDPE), 2) polyvinyl chloride (PVC) and 3) a geosynthetic clay liner (GCL). From the quoted values, it is possible to estimate the potential cost of capping the tailings with a geomembrane and a 40 cm protective covering (Table VII-1). These estimates were based on an area of 100 ha. A range of prices is shown for each material due to the variance in cost for different thickness of the cover. The prices for sand, gravel and topsoil were provided by Two Way Enterprises Ltd. of Yellowknife (Two Way, 1998) and are subject to availability. The range given for the total cost was calculated using the least (PVC – 30 mil) and the most expensive (HDPE – 80 mil and GCL). These and subsequent cost estimates are based on Canadian dollars.

The GCL is capable of being the sole hydraulic barrier component and is capable of achieving lower hydraulic conductivity than 60 to 90 cm of compacted clay liner. This greatly reduces the amount of cover material required. Other benefits over standard clay liners include a reduction in negative effects caused by freeze/thaw and drying/rewetting cycles, and cracking under differential settlement (Nilex Product Information).

Table VII-1: Cost estimate for geomembranes from Nilex Inc.

Material	**Thickness (mil)**	**Installation Rate (m^2/day)**	**Cost (\$/m^2)**	**Actual Cost (\$)**
HDPE	40 – 80	7000	5.5 – 8.5	5 500 000 – 8 500 000
PVC	30 – 40	10 000	5 – 6.25	5 000 000 – 6 250 000
GCL	N/A	10 000	7 – 8.5	7 000 000 – 8 500 000
Cover	**(cm)**	**Volume (m^3)**	**(\$/m^3)**	
sand	10	100 000	11.04	1 104 000
gravel	20	200 000	13.55	2 710 000
topsoil	10	100 000	26.16	2 616 000
Total				**11 430 000 – 14 930 000**

In this case, a protective liner (sand, clay or a geotextile) below the geomembrane is not required. The geomembrane can be placed directly upon the tailings as long as all foreign material is removed and the tailings represent a smooth surface (Kehler, 1998). During this process, the grade of the mine tailings should be adjusted to 3-5%. This minimizes the possibility of pooling of water on the geomembrane due to slope changes (Bathurst, 1993).

For all three materials, a covering is required to help reduce damage to the membrane by sunlight, animals and roots. The amount of water reaching the geomembrane will be reduced by increased evaporation. The thickness of this covering material can be kept to a minimum since the forecasted future use of the tailings ponds does not include vehicles and heavy machinery. Therefore, a 30 cm cover was recommended by Nilex. To reduce the possibility of puncturing the liners, a 8-10 cm layer of sand should be placed directly upon the HDPE and PVC liners. For the GCL, the material in direct contact should not have sharp edges and be no greater than 2 cm in diameter. However, since no cost savings will be realized by not using the sand layer as it is less expensive then gravel, it is still recommended as an added precaution.

The topsoil layer is generally used to further reduce erosion and the amount of water reaching the geomembrane, not to mention for esthetic reasons. The 10 cm thickness of topsoil is a very conservative estimate in comparison to other more southern locations. Topsoil depths may range from 20 cm at a landfill in New Jersey (Pollution Online, 1997), 30 cm at the Eagle Mine in Colorado (Neukirchner and Parachini, 1993) and the 60 cm recommended by the US EPA. It is believed that less topsoil would still allow for sufficient plant growth due to the more northern location of this site. The cost of seeding the topsoil with the correct species of plants has not been included.

The semi-arid weather conditions in Yellowknife (average annual precipitation of 259 mm (WeatherPost, 1998)) may allow for the elimination of the topsoil layer. A gravel layer may be sufficient to reduce the erosion of the sand layer even during the period of spring runoff (Feeney, 1991). In addition, a filter layer is often required below the topsoil layer to prevent the fine-grained soil from entering and clogging the drainage layer (Christopher, 1991). This would further increase the cost, and the amount of required topsoil may easily surpass the supply within the Yellowknife area.

A potential cost savings could be achieved by substituting washed tailings solids or flotation tailings produced by the mine for a portion of the cover layer. This material may support vegetation growth (Royal Oak, 1997). For this material to be placed directly over the geomembrane, it would have to have sufficient drainage capabilities to minimize pooling of water. Prior to a decision on the composition of the protective layer, field experiments should be conducted to ensure erosion of the layer will not occur. This investigation could be conducted without the use of a geomembranes and could include an attempt at introducing vegetation.

For the determination of the proper vegetation cover, a variety of factors need to be investigated. The physical and chemical properties of the tailings or cover material will influence the choice of plant species. The chosen vegetation cover should be able to survive in the long term without the addition of further amendments. For this to occur, native species are recommended as they are already adapted to the climactic conditions of the area. However, the availability of seeds may not be sufficient. Therefore, domestic species that are available, cost effective, and easy to grow with amendments, may be used. Over time, these domestic species generally die off to be replaced by native species. Regardless of the species, amendments such as fertilizers, lime, organics and mulches may be required to promote growth (MNDM, 1994).

b) Simple Gravel Cover

A simpler cap for the tailings ponds can be constructed without the use of geomembranes. This option is more dependent on the local availability of material as the cost of transportation of the required material over long distances would be prohibitive.

A possible example would be the cap design used on the Eagle Mine in Colorado. At this site, they have consolidated 7 million tonnes of tailings within one area. The capping method was designed to reduce any contact the tailings have with air, water, humans and wildlife. The cap would reduce the migration of metals into the groundwater. The cap consists of a 15 cm low-permeability layer, a 60 cm erosion layer and a 30 cm growth medium layer. The area was then seeded with natural grasses (Neukirchner and Parachini, 1993). The plants absorb a large portion of the water reducing erosion, water runoff and groundwater contamination (O'Brien and Neary, 1981; Flaherty, 1996).

The immediate downside to this method is the local unavailability of low permeability clay within the Yellowknife area, as was confirmed by Two Way Enterprises Ltd. The cost to truck in the 150 000 m^3 required for a 15 cm layer would be prohibitive. Therefore, the use of clay for a low-permeability layer is not considered to be feasible. If these depths were used to cover the Giant Mine tailings areas, 150 000 m^3 of low-permeability material, 600 000 m^3 of gravel and 300 000 m^3 of topsoil would be required. The pure volume of this is prohibitive.

The minimization of water infiltration into the tailings may be difficult without the availability of natural clay. Depending on their hydraulic conductivity, the washed tailings solids or flotation tailings may have the proper characteristics to divert large amounts of surface water away from the contaminated tailings. For this to occur, the final construction would have to ensure a sufficient grade to promote water runoff. If these materials were used, a subsequent layer (gravel) would be required to reduce wind and water erosion.

To simply reduce water and wind erosion of the tailings, the tailings ponds could be covered with a 20 cm layer of gravel as per the cover for the geomembranes. This would cost approximately $2 710 000 (Table VII-1).

c) Do Nothing Option

Doing nothing is not recommended in this situation because the tailings will continue to be a source of future contamination due to the three possible pathways of redistribution: wind erosion, water runoff and contamination of the groundwater. If a cleanup of the mine site and other contaminated areas is completed, the tailings would likely recontaminate all of the cleaned areas if they were not dealt with. Therefore, any efforts spent on reducing contaminant levels in Yellowknife Bay and Baker Creek may be counteracted if the tailings ponds are left as is.

B. Yellowknife Bay and Beach Area

As shown in the loading calculations (Table VI-8), large areas of Yellowknife Bay contain abnormally high concentrations of arsenic, especially the Baker Creek outlet area within Yellowknife Bay and the Beach Tailings Area. Dredging of the contaminated sediments is proposed as a possible solution if it is determined that the contaminants pose a sufficient threat to environment to justify reclamation. The USEPA considers dredging an effective method and has used this technique at a number of sites (USEPA, 1998). Two other possible techniques for the reclamation of contaminated sediments, which have been used successfully by the USEPA, are sediment solidification and capping (USEPA, 1991). Sediment solidification was not considered due to its higher cost and energy requirements. Capping was not considered due to the possibility of the upward flux of the arsenic through the capping layer into the water column and the limited availability of low permeability clay within the area.

Three companies with expertise in environmental dredging were contacted for information on costs and modes of operation. General site specific information was given to these companies to help them determine rough cost estimates. For more accurate estimates, the exact location of the site would have to be disclosed in order to allow perform site visits. The location of the site was given as approximately 1500 km north of Edmonton by road. Costing estimates were done with the assumption of 120 000 m^3 of sediments to be dredged from Yellowknife Bay at a depth of 15 cm, and 32 000 m^3

from the Beach Tailings Area at a depth of 20 cm. The depth for Yellowknife Bay was chosen in order to ensure that the heavily contaminated surface sediments were removed. The 20 cm for the Beach Tailings Area is taken as the estimated average depth throughout the entire area. The dredged sediments could possibly be disposed of in the South Tailings Ponds. The could be moved to the other tailings ponds if the South Pond is too full. The static lift to the South Pond was estimated at 30 m. The distances required to pump the sediments from Yellowknife Bay and the Beach Tailings Area to the South Pond were set at 1500 m and 500 m, respectively.

Northern Underwater Systems Ltd. (NUS) of Ardrossan, Alberta was contacted (Leonard, 1998). Information provided by him consisted of general cost estimates for the removal of one cubic yd of sediment based on a hydraulic method for sediment removal (Table VII-2) (Leonard, 1998). The days required for dredging would have to be split between summer seasons.

Table VII-2: Northern Underwater Systems dredging cost estimate.

	$\$/m^3$	m^3/day	Beach Area Cost ($)	Days	Yellowknife Bay Cost ($)	Days	Total Cost ($)
Minimum	4.75	240	260 000	91	973 000	341	1 233 000
Maximum	7.10	350	387 000	135	1 452 000	506	1 839 000

Forth Dynamic Inc. of Edmonton, AB (Trepanier, 1998) recommended using a cutter suction dredge at this site because it will minimize the resuspension of sediments. They contacted the environmental dredging firm, Land Marine Pile & Dredge from Kelowna, BC, who provided the cost estimates.

Table VII-3: Land Marine Pile & Dredge dredging cost estimate.

	$\$/m^3$	Set-up and Breakdown ($)	Beach Area Cost ($)	Yellowknife Bay Cost ($)	Total Cost ($)
Minimum	8	200 000	456 000	1 160 000	1 616 000
Maximum	12	200 000	584 000	1 640 000	2 224 000

A thorough cost estimate was furnished by Ceda-Reactor Inc. of Calgary, Alberta (Clement, 1998). Ceada-Reactor Inc. uses a Mud Cat^{TM} dredge, which is built by Ellicot International. The effectiveness of this dredge was shown by the Contaminated Sediment Removal Program (Environment Canada, 1998), which investigated various technologies for the removal of sediments from polluted areas of the Great Lakes. Field testing was conducted on various technologies which met and surpassed the set standards of operation and performance. These standards are:

- Turbidity: To not exceed ambient levels by >30%, 25 m from operation
- Suspended Solids: For ambient levels <100 mg/L, the ambient levels cannot be exceeded by >25 mg/l, 25 m from operation. For areas with ambient levels >100 mg/L, the ambient levels cannot be exceeded by >10%, 25 m from operation
- Total Organic Carbon: To not exceed 27 mg/l, 25 m from operation. Where ambient levels >27 mg/l, not to exceed it by >30%.
- Overflows and Leaks: Holding facility for excavated sediment must have a minimum freeboard of 1 m and be sealed for transport.
- Removal Efficiency: To not exceed solids to liquid ratio >30% by volume.
- Effluent Quality: The slurry mixtures should allow for the removal of suspended solids and treatment of effluent.
- Production Rate: Should allow for sufficient settling time in holding area.

Three technologies surpassed these criteria with the Mud Cat MC 915 ENV being one of them. The Mud Cat can be readily modified to meet any specific environmental criteria needed for a site.

The cost estimate furnished by Jos Clement was more site specific and required more detailed information. For crew costs, 3 personnel would be required with accommodation at a local hotel for $100/night. The cost estimate (Table VII-4) is based on 16 hours of operation per day, which can be increased if required. It also includes the cost of fuel based on 53 L/hr at $0.70/L.

Table VII-4: Ceda-Reactor dredging cost estimate

Area	$/m^3	Cost ($)	m^3/day	Days
Beach	5	175 000	1224	26
Yellowknife Bay	6	778 000	1224	98
Total		**953 000**		

Transportation costs and crane rental are not included in these totals. The cost of transporting all necessary equipment from Calgary to Yellowknife is estimated at $11 200 each way for five transport trucks from Northern Industrial Carriers Ltd., Calgary, Alberta. A one-day period is required to get the equipment in and out of the water with an estimated set-up time of 7 days. A 50-ton crane is required for one day during the set-up and tear-down procedures, and can be rented from Territorial Crane Service in Yellowknife at $170/hr for a total cost of approximately $2720.

The sediments would be transported to the South Pond by an 8" plastic pipe. The large distances and the change in elevation requires two boosters for Yellowknife Bay and one for the Beach Area to provide sufficient power. The large distance and changes in elevation affect the removal efficiency, which is estimated at 10%. Jos Clement believes that silt curtains would not be required to minimize the redistribution of sediments during the dredging process. This will depend on the specific criteria set for this site and the characteristics of the sediments. This technique is recommended because it costs less, requires less time and is a proven technology.

Prior to any work on the Beach Tailings Area, it is recommended that the tailings on shore between the water and the southern edge of the South Pond be removed and placed into the tailings ponds. These tailings pose a continual threat of further contamination. They are situated in a natural water runoff zone, which is susceptible to erosion. The dredging of the Beach Area could be completed prior to the closure of the mine since it is not being directly affected by current mining operations.

For Yellowknife Bay, dredging should not take place prior to the stoppage of mine operations and any reclamation work to be conducted on the sediments of Baker Creek. The effluent discharge and the sediments of the creek are sources of further contamination for the sediments of Yellowknife Bay.

C. Baker Creek Sediment

A cost estimate has not been determined for this area because a site visit would be required by a contractor as the removal of these sediments is very site specific. The removal of the top 15 cm of sediment throughout Baker Creek from the area of sample #20 near the effluent pipe to sample #22 near the outlet should remove the majority of the arsenic and other contaminants within the creek sediments. The estimated volume of these sediments is 9000 m^3. The cleanup of the creek sediments should occur prior to any cleanup done of Yellowknife Bay sediments due to the possibility of increased contaminated sediment displacement during the sediment removal process. If this cleanup is not done, these sediments will continue to be a source of arsenic contamination through redistribution and bulk transport.

In order to minimize the amount of sediment disturbance with subsequent increased deposition of contaminated sediments into Yellowknife Bay, a number of steps can be taken. First, the removal period should be in late summer early fall when water flow in the creek is at a minimum. The pond near sample #20 could be drained by rerouting the flow of the creek and opening the southern edge to permit increased water flow from the pond. This would allow for the removal of its sediments.

Once completed, a temporary dam would be constructed at the southern end of the pond to minimize the flow of water throughout the creek. This would allow for the removal of sediments throughout the majority of the creek while minimizing redistribution. Standard construction equipment should be sufficient for the removal of these sediments. Once again, they could be disposed of within the tailings ponds.

D. Recommendations

1. A closer investigation of tailings ponds is required with a number of items to be identified:

- Identification of areas of concern for water runoff and erosion of tailings.
- Sampling of the North, Settling and Polishing Ponds to determine if there is a difference in arsenic concentrations and characteristics.
- A complete hydrogeological study to determine the potential for groundwater contamination.
- The determination of the exact form of the arsenic found within the tailings ponds.

2. Further investigation of the extent of arsenic contamination in the area of Yellowknife Bay affected by the Baker Creek outlet is required. The area has not been

adequately sampled to produce an accurate picture of the concentration of contaminants at the surface and at depth.

3. A detailed investigation into the speciation of the arsenic and its toxicological effects upon the local environment is required to determine if the arsenic present is having a detrimental effect.

4. A detailed loading investigation needs to be conducted for the Beach Area to answer a number of outstanding issues. How much tailings material is present between the Beach Area and the South Pond? What is the depth and extent of direct tailings coverage within Yellowknife Bay? To what degree have the Beach Tailings affected the remaining natural sediments in the area?

5. For reclamation purposes, the various methods of covering the tailings need to be further investigated. The extent that these tailings are to be isolated from the environment needs to be determined.

VIII. CONCLUSIONS

1. Aim

The aim of this thesis was to assess the overall extent of arsenic contamination due to the operations of the Giant Mine. This process included method development for the analysis of high levels of arsenic by XRF, the determination of background arsenic concentrations, the area affected by anthropogenic discharge, and the potential bioavailability of the arsenic in the tailings and the sediments. This information allowed for an initial assessment of reclamation areas within the study area, and of a variety of possible solutions.

2. Method Application – XRF

In order to minimize the time and cost of arsenic analysis of sediments, a TN Spectrace 9000 XRF was calibrated for arsenic analysis. The calibration showed linear results to at least 10 000 ppm for arsenic. Results obtained by XRF and the more traditional NAA and AA methods were compared showing that a good correlation between the results obtained by NAA and XRF. Overall, the XRF was proven to be an effective method of analysis of total arsenic at concentrations greater than 120 ppm with the capability of reducing both cost and time required for analysis.

3. Extent of Arsenic Contamination

The fact that the area surrounding the Giant Mine is contaminated with high arsenic levels is not a new development. This study, however, revealed several new factors and clearly demonstrated the extent to which the mine has influenced the study area. Arsenic concentrations were determined for the first time in Baker Creek, the Beach Tailings and the tailings ponds. It was found that the sediments and water column of Baker Creek, which receives the effluent discharge, are highly contaminated. The flow of the creek into Yellowknife Bay was shown to increase the arsenic concentration within the sediments of the Bay.

The results allowed for a preliminary estimate of the amount of arsenic found within the area. The ≈200 000 tonnes of arsenic trioxides located in the mine shafts and the determined 41 400 tonnes of arsenic within the tailings ponds far surpass what the contaminated areas are estimated to contain. It was estimated that there are currently 12, 51 and 44 tonnes of arsenic are found in Baker Creek, its outlet area, and the Beach Tailings Area, respectively.

For the first time, all of the components of the arsenic cycle in Yellowknife Bay comprising the sediment, porewater and water column, were investigated. This included the concentrations of arsenic in the water column and the concentration of arsenic, manganese, and iron in sediments and porewater. The information was used in conjunction with sediment concentrations of a number of other elements (Au, Ca, Co, Cu, K, La, Na, Ni, Sb and Zn) to determine whether the majority of the contaminants in the study area are anthropogenic or natural.

It was concluded that the majority of the arsenic contamination was due to anthropogenic sources with arsenic from natural sources contributing only a small amount of the arsenic within the study area. The sediments at greater depth were found to approach background concentrations.

Sample location #1 has been unaffected by the nearby anthropogenic discharge of contaminants with its arsenic concentration of 6 ppm. The background arsenic concentration within Yellowknife Bay and Baker Creek was found to be within the range of 7 to 25 ppm and 41 to 104 ppm, respectively.

Anthropogenic sources include aerial emissions and effluent discharge with arsenic in the dissolved or particulate form. Aerial emissions have contributed 20700 tonnes of arsenic trioxide to the local environment. Their emissions may have contributed to the elevated levels of arsenic found throughout Yellowknife Bay, but they are not the dominant source of the highly contaminated areas within Baker Creek and its outlet into Yellowknife Bay.

The majority of the remaining arsenic entering the environment is in the dissolved form. This conclusion was reached as a result of sequential extraction tests, which showed that the majority of the arsenic within the sediments is bound to Mn and Fe oxides. Upon entering the environment, this dissolved arsenic is adsorbed onto and/or co-precipitates with the naturally occurring iron and manganese oxides. Redistribution of arsenic can also readily occur by the flux of arsenic from the sediments into the water column. The contaminated sediments of Baker Creek are also likely to undergo bulk transport followed by deposition into Yellowknife Bay due to the water current in the creek.

Leachate tests and porewater analyses confirmed that arsenic is not permanently bound to the sediments and has the capability of leaching into the environment. Sample location #20 is categorized as leachate toxic waste by Reg. 347 from the MOEE. Analysis of porewater revealed arsenic concentrations up to 3371 ppb. Thus, in conjunction with the determined upward flux of arsenic, it is apparent that the arsenic currently within the sediments is capable of re-entering the environment.

Definite differences were found in the stability of the tailings and sediment samples. Oxides were the dominant phase within the sediments where the residual phase was dominant in the tailings. This showed that the arsenic within the tailings is not as available as the arsenic within the sediments. However, the total amount of arsenic in the other four more bioavailable phases averages 1000 ppm. The leachate test further confirmed the difference between the sediment and tailings samples. The average arsenic concentration within the tailings was 300 ppm greater than the sediments, however, the average leachate concentrations were 130 ppb for the tailings and 4300 ppb for the sediments.

4. Recommendations for Reclamation and Future Study

This study focussed on total arsenic concentrations, which were then compared to appropriate criteria concentrations. This comparison supports the potential for toxic effects from anthropogenic sources of arsenic. It should be stressed, however, that arsenic toxicity is strongly linked to chemical form and final conclusions should await the results of a detailed study of arsenic speciation. Given the public concern regarding arsenic contamination, an evaluation of possible cleanup options, and their associated costs, was considered useful.

The areas of immediate concern are the Beach Tailings Area and the sediments of Baker Creek and its outlet area into Yellowknife Bay. The potential for the redistribution of arsenic in these areas is high as they are located in the environment and the possibility for redistribution has been established.

The Beach Tailings Area comprises of an estimated 32 000 m^3 of tailings within Yellowknife Bay. The amount of tailings on land is unknown, but the erosion of these tailings into the Bay is ongoing. Within Baker Creek, the top 15 cm of sediments are highly contaminated comprising an estimated 9000 m^3 of sediments. The heavily contaminated sediments within the outlet area in Yellowknife Bay consists of roughly

120 000 m^3 extending to a depth of 15 cm. A possible reclamation solution would be the dredging of these sediments and tailings, and placing them in the existing tailings ponds. The total cost of dredging the tailings and contaminated sediments from Yellowknife Bay is estimated at $978 000 (Ceda-Reactor Inc.).

The tailings ponds can cause future contamination by leaching into the groundwater, by wind erosion, and by water erosion. To prevent this, the feasibility of a variety of different covers has been investigated. Possible covers include using a geomembrane of PVC, HDPE or GCL with 40 cm of cover material at a cost ranging from $11 400 000 to $14 900 000 (Nilex). This would all but eliminate any water and wind erosion. A more simple cover would consist of a 20 cm layer of gravel. This would prevent wind erosion and help reduce water erosion, at a cost of $2 700 000. At this time, a specific cover cannot be recommended without further on-site study. The suitability of other possible cover materials such as the washed tailings solids or flotation tailings need to be investigated further.

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X. APPENDICES

A. Analytical Results

Table X-1: Analysis of spiked silica sand samples for XRF calibration (Figure V-1).

Arsenic (ppm)	**100**	**150**	**500**	**1000**	**2000**	**3000**
Reading	164	197	596	1116	2138	3185
	158	192	618	1093	2135	3484
	154	193	618	1104	2174	3219
	160	206	582		2244	3165
Avg Reading	159	197	604	1104	2173	3263
Std Dev	4	6	18	12	51	149
Rel Std Dev	2.6	3.2	2.9	1.0	2.3	4.6
Arsenic (ppm)	**4000**	**5000**	**6000**	**7000**	**8000**	**10000**
Reading	4463	5579	6542	7615	9523	11045
	4470	5660	6476	7730	9255	10891
	4531	5678	6696	7740	9508	10826
	4420	5538	6679	7888	9498	
Avg Reading	4471	5614	6598	7743	9446	10921
Std Dev	46	66	107	112	128	112
Rel Std Dev	1.0	1.2	1.6	1.4	1.4	1.0

Table X-2: Analysis of spiked Yellowknife Bay sediments (sample location #1) for XRF calibration

Arsenic	**1000**	**2000**	**3000**	**5000**
Reading	1262	2347	3496	5870
	1190	2574	3742	5997
	1251	2566	3764	6289
	1333	2583	3895	6408
	1374	2562	3518	6406
Avg Reading	1282	2526.4	3683	6194
Std Dev	72	101	171	247
Rel Std Dev	5.6	4.0	4.6	4.0

Table X-3: XRF Analysis of the certified reference material, PACS-1 (ppm).

	As	Cu	Mn	Sb	Zn
Certified Value	211 ± 11	452 ± 16	470 ± 12	171 ± 14	824 ± 22
Determined Values	192	326	470	133	470
	165	305	440	118	557
	205	289	470	106	525
	214	332	480	125	505
Average	194	313	465	120.5	514.25
Std Dev	21.3	19.7	17.3	11.4	36.5
Rel Std Dev	11.0	6.3	3.7	9.5	7.1

Table X-4: Comparison of XRF, NAA and AA readings for arsenic (Figure V-2).

Sample	Arsenic (ppm)		
	NAA	XRF	AA
3	1016	1038	
4	3140	3623	
8	194	324	
9	398	525	
10	278	390	
16	1764	1914	1263
17	1946	2150	1659
18	2838	4186	1880
19	3821	3523	2412
20	1736	2332	1280
21	1193	1428	239
22	1825	2197	1090
25	302	509	
27	738	839	531
28	974	1260	
29	114	229	50
BC-30	238	206	
30	3494	3703	3263
31	4842	4960	3621
32	3072	3312	1032
33	1738	1931	1650
34	2808	3019	2666
35	2740	3025	2102
36	2730	2907	2248
37	3301	3058	2241
38	3480	3225	2795
39	4431	3489	
44	1919	1200	
45	1643	1677	
22 - 0/0.5	1310	1580	
22 - 1/1.5	1173	1452	
22 - 2/2.5	1022	1170	
22 - 2.5/3	956	1084	
22 - 3/3.5	725	757	
22 - 3.5/4	514	574	
18 - 0.5/1	608	725	

Table X-5: Remaining data used for the PCA on sediments down core based on XRF analysis (ppm) (Figure VI-4).

Sample	As	Fe	Mn	Zn	Cu	Sb	K	Ca
3	1038	31120	1460	108	55	42	9870	68850
6	200	26960	900	116	44	0	26140	13250
8	324	33690	1010	184	237	87	27420	13190
10	390	25530	170	183	138	67	24800	12820
16	1914	36480	970	260	450	187	21380	20300
19	3692	42403	990	253	273	289	21170	24877
23	173	31753	2260	112	88	25	28070	13503
24	149	19060	1020	99	45	0	21360	15470
26	147	29430	810	74	53	0	29170	27020
28	1260	32870	1370	159	71	84	12623	77153
29	229	27710	1320	62	75	31	26670	15010
BC-30	306	25180	740	101	55	194	27090	17320
30	3703	71540	1480	365	289	319	16440	68810
31	4960	82380	1790	600	462	332	18060	61460
32	3312	66977	1807	320	280	339	16197	67793
33	1931	62800	2200	157	77	166	12090	68040
34	3019	56260	1553	412	169	235	19917	65317
35	3025	61390	1840	263	36	232	19960	70290
36	2907	53770	1770	206	65	255	18940	68800
37	3058	64720	1170	185	76	159	13860	65000
38	3225	65160	1760	343	60	403	15790	68300
39	3489	68697	1647	295	104	330	11993	66253
44	2000	63920	1480	328	243	37	14080	69110
45	1677	61420	1700	252	115	40	12390	73630

Table X-6: Remaining data used for the PCA on sediments down core based on NAA analysis (ppm) (Figure VI-5).

Sample	As	Fe	Zn	Sb	Au	K	Na	La
3	1016	38800	150	39.4	3.401	9300	3370	4.04
4	3140	43000	330	201	4.7	25000	16140	27.2
8	194	41400	185	32.7	1.37	23400	16900	41.6
9	398	40900	134	18.5	0.708	22800	17520	37.9
10	278	29400	157	62.9	1.869	19100	15200	36.1
16	1764	41100	295	208	5.87	18300	12660	24.87
17	1946	35500	182	122	2.673	21600	17820	28.2
18	2838	31000	192	441	22.67	18500	8786	22.42
19	3821	51660	298	301	13.25	29200	11500	23.6
20	1736	19700	228	182	6.251	18500	17280	27.98
21	1193	41300	192	66.4	1.233	25900	14470	36.94
22	1825	39200	345	235	3.871	5659	4846	19.646
23	88.07	40600	128	5.48	0.3039	23300	15880	45.38
24	41.36	24500	67	1.3	0.0071	17200	19290	24.82
25	301.6	47300	200	15.1	0.73	22400	14400	45.3
26	64.596	36600	109	5.43	0.0485	25200	13010	49.23
27	738	35800	140	46.41	1.746	9165	3143	3.958
28	974	38000	198	66.59	1.78	10100	3003	3.53
29	114	37600	116	4.68	0.0229	22300	16810	42.39
30	237.6	30800	96	205.3	0.3469	25000	18620	38.51
30	3494	82200	454	413	1.163	18200	4758	8.93
31	4842	96400	739	432	1.381	13500	3962	8.729
32	3072	78800	483	326	0.855	14700	4859	8.39
33	1738	65500	187	125.7	1.12	10200	3126	4.791
34	2808	69970	483	245	1.145	18500	4219	7.32
35	2740	72800	306	246.7	1.0581	18500	3508	6.15
36	2730	63600	242	238.6	1.606	15900	6028	5.365
37	3301	73400	256	88.5	1.647	11500	4002	7.82
38	3480	82800	325	354	16.846	13000	5151	7.67
39	4431	76000	326	299.5	3.06	13400	5807	8.86
44	1919	82100	480	23.2	0.92	12700	4850	20.3
45	1643	75800	324	19.5	0.8	10000	7980	13.7

Table X-7: Arsenic concentrations in surface water (VI-1).

Sample	Arsenic (ppb)	Sample	Arsenic (ppb)
30	10854	**27**	67
31	11236	**3**	2.6
29	175	**9**	1.3
24	52	**9-4.5**	1.4
20	102	**9-9**	1.3
18	276	**23-0**	2.4
22	114	**23-6**	3.0
4	55	**23-12**	2.3
4-3	2.4	**25-0**	2.8
21	1.7	**25-5**	1.7
21-5.5	2.9	**25-11**	11.4
21-11	0.9	**Tap**	0.8

Table X-8: Arsenic concentrations of the leachate tests and the corresponding sediment samples (VI-8).

Sample	Leachate (ppb)	Sediment (ppm)
4	2442	3140
18	127	2838
20	9700	1736
3	8	1016
27	51	738
28	1583	974
30	11	3494
31	201	4942
32	38	3072
33	263	1738
34	24	2808
35	3	2740
36	94	2730
37	532	3301
39	184	4431

B. Quality Assurance / Quality Control

The extraction procedure was conducted on two different portions of the same sample for AA analysis (Table X-9). This confirms the reproducibility of the extraction procedure and the analytical technique.

Table X-9: Duplicate AA analysis of sediment samples (ppm).

Samples	Cu	Mn	As	Fe	Ni	Co
1		399			27	9
		285			31	9
Average		342			29	9
Std Dev		80.6			2.6	0.5
Rel Std Dev		23.6			9.2	5.6
3	20	1179	619	18057	28	7
	20	1281	491	36612	24	7
Average	20	1230	555	27334	26	7
Std Dev	0.1	72.0	90.5	13120.0	3.4	0.1
Rel Std Dev	0.4	5.9	16.3	48.0	13.2	1.9
4	239	334	639	24117		
	251	361	547	10734		
Average	245	348	593	17425		
Std Dev	8.4	18.8	64.9	9462.9		
Rel Std Dev	3.4	5.4	10.9	54.3		
9	59	1124	445	33018		
	60	1144	418	33684		
Average	60	1134	432	33351		
Std Dev	0.7	14.4	19.1	470.6		
Rel Std Dev	1.2	1.3	4.4	1.4		
17	171	402				
	169	399				
Average	170	401				
Std Dev	1.2	2.8				
Rel Std Dev	0.7	0.7				
18	249	798	1460	23664	227	101
	209	795	1668	8632	177	81
Average	229	796	1564	16148	202	91
Std Dev	28.7	1.8	146.5	10628.9	34.9	14.3
Rel Std Dev	12.5	0.2	9.4	65.8	17.3	15.7
21	312	1610	638	41982	62	20
	298	1786	868	39578	60	18
Average	305	1698	753	40780	61	19
Std Dev	10.2	124.0	162.6	1699.4	1.5	1.2
Rel Std Dev	3.3	7.3	21.6	4.2	2.5	6.6

Table X-9 (cont'd): Duplicate AA analysis of sediment samples (ppm).

Samples	Cu	Mn	As	Fe	Ni	Co
23	82	1452	157	32326		
	78	1521	189	33882		
Average	80	1486	173	33104		
Std Dev	2.5	49.2	22.6	1100.4		
Rel Std Dev	3.2	3.3	13.1	3.3		
25	59	1129	161	34296		
	59	1302	170	34306		
Average	59	1216	166	34301		
Std Dev	0.2	122.6	6.4	7.3		
Rel Std Dev	0.4	10.1	3.8	0.0		
27-20		1068			30	5
		817			31	8
Average		942			31	7
Std Dev		177.9			0.6	1.6
Rel Std Dev		18.9			1.9	24.3
35	64		2102		81	30
	72		2342		90	30
Average	68		2222		85	30
Std Dev	5.5		169.6		5.8	0.0
Rel Std Dev	8.1		7.6		6.7	0.1
36	47		2248		67	24
	43		2148		80	22
Average	45		2198		73	23
Std Dev	2.8		71.0		9.3	1.3
Rel Std Dev	6.2		3.2		12.8	5.6
45	102	1130			69	29
	119	1071			76	28
Average	110	1100			72	28
Std Dev	12.5	42.0			4.9	0.7
Rel Std Dev	11.3	3.8			6.8	2.4
Avg Std Dev	6.6	64.2	84.0	5212.8	7.9	2.5
Avg Rel Std Dev	4.6	7.3	10.0	25.3	8.8	7.8

Table X-10: Analysis of certified reference material by AA.

Mess-2: Marine Sediment						1646 - Estuarine Sediment
	Cu	Mn	As	Ni	Co	Fe
Certified Value	39.3 ± 2.0	365 ± 21	20.7 ± 0.8	49.3 ± 1.8	13.8 ± 1.4	33500 ± 1000
	30	321	21	30	7	29457
	40	338	24	31	7	28404
	33	284	12	49	5	28579
	34	299	12	51	11	28576
	35	261		51	9	
	39	250		49	10	
Average	35	292	17	43	8	28754
Std Dev	3.7	33.9	6.3	10.2	2.3	475.7
Rel Std Dev	10.6	11.6	36.4	23.5	29.2	1.7

Table X-11: The range of detection limits for NAA analsysis.

	Lower Limit (ppm)	Upper Limit (ppm)
Au	0.004	0.05
As	0.6	14
Fe	900	5400
K	540	16200
La	0.20	1.6
Na	17	230
Sb	0.14	1.0
Zn	10	30

Homogeneous portions of dried and ground sample were given to the personnel of the Analytical Services Group. Five samples were analyzed in duplicate.

Table X-12: Duplicate samples from NAA analysis (ppm).

Sample	Au	As	Fe	K	La	Na	Sb	Zn
16	5.87	1765	4.11	1.83	24.9	1.266	208	295
	5.94	1849	4.22	1.72	25.4	1.366	217	304
Average	5.91	1807.0	4.2	1.8	25.2	1.3	212.5	299.5
Std Dev	0.05	59.4	0.1	0.1	0.4	0.1	6.4	6.4
Rel Std Dev	0.8	3.3	1.9	4.4	1.4	5.4	3.0	2.1
28	1.78	974	3.8	1.01	3.53	0.3	66.6	198
	1.781	981	3.63	0.98	3.5	0.29	67	204
Average	1.78	977.5	3.7	1.0	3.5	0.3	66.8	201.0
Std Dev	0.00	4.9	0.1	0.0	0.0	0.0	0.3	4.2
Rel Std Dev	0.0	0.5	3.2	2.1	0.6	2.4	0.4	2.1
32	0.889	3190	7.97	1.47	8.4	0.486	326	483
	0.898	3230	8.64	1.57	8.92	0.535	344	459
Average	0.89	3210.0	8.3	1.5	8.7	0.5	335.0	471.0
Std Dev	0.01	28.3	0.5	0.1	0.4	0.0	12.7	17.0
Rel Std Dev	0.7	0.9	5.7	4.7	4.2	6.8	3.8	3.6
39	3.06	4430	7.6	1.34	8.87	0.581	300	326
	2.838	4400	7.31	1.3	8.1	0.582	298	357
Average	2.95	4415.0	7.5	1.3	8.5	0.6	299.0	341.5
Std Dev	0.2	21.2	0.2	0.0	0.5	0.0	1.4	21.9
Rel Std Dev	5.3	0.5	2.8	2.1	6.4	0.1	0.5	6.4
22-10/11	0.0841	46.9	2.47	2.2	35.9	1.859	6.03	98
	0.092	53.4	2.33	2.16	35.4	1.878	6.25	98
Average	0.09	50.2	2.4	2.2	35.7	1.9	6.1	98.0
Std Dev	0.01	4.6	0.1	0.0	0.4	0.0	0.2	0.0
Rel Std Dev	6.3	9.2	4.1	1.3	1.0	0.7	2.5	0.0
Avg Std Dev	0.04	23.7	0.2	0.05	0.3	0.03	4.2	9.9
Avg Rel Std Dev	2.7	2.9	3.5	2.9	2.7	3.1	2.0	2.9

Table X-13: NAA analysis of certified reference materials.

Reference Material	Au (ppm)	As (ppm)	Fe (%)	K (%)	La (ppm)	Na (%)	Sb (ppm)	Zn (ppm)
Mess - 1: Marine Sediment (NRCC)								
Certified Value		20.7 ± 0.8	4.35 ± 0.22				1.09 ± 0.13	172 ± 16
Determined		19.3	4.07				1.16	145
Values		20.6	4.44				1.38	187
		20	4.4				1.21	179
		19.9	4.63				1.16	
Average		20.0	4.4				1.2	170.3
Std Dev		0.5	0.2				0.1	22.3
Rel Std Dev		2.7	5.3				8.5	13.1
GSD - 9: Stream Sediment (Republic of China)								
Certified Value		8.4 ± 0.4	3.40 ± 0.03	1.65 ±0.025	40 ± 2	1.07 ± 0.02	0.81 ±0.08	78 ± 2
Determined		8.79	3.6	1.68	41.1	1.108	0.9	96
Values		8.25	3.3	1.57	39.8	1.084	0.97	100
		8.7	3.58	1.59	40.2	1.087	1.02	92
		8.74	3.56	1.65	41.3	1.108	0.9	
Average		8.6	3.5	1.6	40.6	1.1	0.9	96.0
Std Dev		0.2	0.1	0.1	0.7	0.0	0.1	4.0
Rel Std Dev		2.9	4.0	3.2	1.8	1.2	6.2	4.2
GSD - 10: Stream Sediment (Republic of China)								
Certified Value		25 ± 1	2.70 ± 0.03	0.10 ±0.006	13.0 ± 0.5		6.3 ±0.3	46 ±2
Determined		23.1	2.71	0.101	12.42		5.47	65
Values		24.2	2.7	0.102	12.83		5.65	65
		23.9	2.83	0.103	12.48		5.74	54
		22.9	2.7	0.088	11.96		5.45	
Average		23.5	2.7	0.1	12.4		5.6	61.3
Std Dev		0.6	0.1	0.0	0.4		0.1	6.4
Rel Std Dev		2.7	2.3	7.2	2.9		2.5	10.4
GXR – 1								
Certified Value	3.3	427		0.05	7.5	0.05	122	760
Determined	3.40	437		0.052	8.34	0.049	118	670
Values	3.30	423		0.096	8.23	0.049	111	645
	3.21	412		0.033	7.71	0.048	110	
Average	3.3	424.8		0.1	7.9	0.0	115.3	691.7
Std Dev	0.1	10.3		0.0	0.4	0.0	5.7	60.5
Rel Std Dev	2.3	2.4		46.6	5.1	2.0	5.0	8.7

Table X-13 (cont'd): NAA analysis of certified reference materials.

Reference Material	Au (ppm)	As (ppm)	Fe (%)	K (%)	La (ppm)	Na (%)	Sb (ppm)	Zn (ppm)
GSD - 11: Stream Sediment (Republic of China)								
Certified Value		188 ± 6	3.07 ± 0.03	2.72 ±0.025	30 ± 1	0.34 ± 0.01	14.9 ± 0.7	373 ± 6
Determined Values		190.3	3.24	2.81	29.8	0.34	14.5	361
		182.1	3.18	2.56	28.4	0.323	14.4	397
		184.1	3.24	2.65	29.4	0.334	14	330
		188.3	3.41	2.78	30.4	0.34	14.2	
Average		186.2	3.3	2.7	29.5	0.3	14.3	362.7
Std Dev		3.8	0.1	0.1	0.8	0.0	0.2	33.5
Rel Std Dev		2.0	3.0	4.3	2.8	2.4	1.6	9.2
GSD - 12: Stream Sediment (Republic of China)								
Certified Value		115 ± 3	3.4 ±0.03	2.42 ±0.02	32.7 ±0.8	0.33 ±0.01	24.3 ±1.3	498 ±8
Determined Values		114.4	3.59	2.35	32.4	0.32	23.6	482
		114.2	3.61	2.425	32.7	0.327	24	478
		110.2	3.5	2.38	31.4	0.316	36.3	
		115.8	3.67	2.39	32.4	0.323	27.9	
Average		113.7	3.6	2.4	32.2	0.3	28.0	480.0
Std Dev		2.4	0.1	0.0	0.6	0.0	5.9	2.8
Rel Std Dev		2.1	2.0	1.3	1.8	1.4	21.1	0.6
GSS - 5: Soil (Republic of China)								
Certified Value	0.26	412 ±8	8.66	1.24 ±0.02	35.7 ±1.8	0.091	35.4 ±2.4	494 ±11
Determined Values	0.21	393	8.66	1.18	33.8	0.066	34.7	504
	0.23	412	8.81	1.25	35.6	0.069	36.3	520
	0.22	390	8.6	1.15	33.5	0.066	34.6	
Average	0.2	401.8	8.7	1.2	34.7	0.1	35.3	506.0
Std Dev	0.0	11.9	0.1	0.0	1.2	0.0	0.8	13.1
Rel Std Dev	8.7	3.0	1.0	4.0	3.4	16.4	2.2	2.6
Avg Std Dev	0.0	4.3	0.1	0.0	0.7	0.0	1.8	20.4
Avg Rel Std Dev	5.5	2.5	2.9	11.1	2.9	4.7	6.7	7.0

The reproducibility of XRF analysis was determined by running the same sample three times. The samples were shaken between the runs.

Table X-14: Duplicate XRF analysis of sediment samples (ppm).

Sample	K	Ca	Mn	Fe	Cu	Zn	As	Sb
4	25450	17960	690	36290	733	338	3596	232
	24260	17880	980	35840	710	304	3548	162
	23610	18400	870	36170	767	286	3726	182
Average	24440	18080	847	36100	737	309	3623	192
Std Dev	933	280	146	233	29	26	92	36
Rel Std Dev	3.8	1.5	17.3	0.6	3.9	8.5	2.5	18.8
17 (June)	23280	19690	1000	28170	172	142	2173	80
	23960	19850	780	28360	175	163	2091	144
	22600	19990	850	29100	176	125	2186	154
Average	23280	19843	877	28543	174	143	2150	126
Std Dev	680	150	112	491	2	19	52	40
Rel Std Dev	2.9	0.8	12.8	1.7	1.2	13.3	2.4	31.9
17-5 (Aug.)	16740	56460	1610	60110	198	617	6380	1224
	17370	57520	1180	59360	230	735	6370	1214
	16670	57820	1210	61210	212	683	6440	1238
Average	16927	57267	1333	60227	213	678	6397	1225
Std Dev	386	715	240	931	16	59	38	12
Rel Std Dev	2.3	1.2	18.0	1.5	7.5	8.7	0.6	1.0
18	21340	24840	1540	35310	354	253	4152	308
	21500	25830	1730	36570	386	252	4179	373
	20530	24560	1170	36520	306	245	4227	325
Average	21123	25077	1480	36133	349	250	4186	335
Std Dev	520	667	285	713	40	4	38	34
Rel Std Dev	2.5	2.7	19.2	2.0	11.5	1.7	0.9	10.1
19	22050	25330	1020	42790	328	283	3719	263
	21340	24780	980	42750	261	221	3651	325
	20120	24520	970	41670	230	255	3707	279
Average	21170	24877	990	42403	273	253	3692	289
Std Dev	976	414	26	635	50	31	36	32
Rel Std Dev	4.6	1.7	2.7	1.5	18.3	12.3	1.0	11.1
23	27920	13670	2000	31690	104	138	177	24
	28520	13410	2340	32270	83	91	157	29
	27770	13430	2440	31300	76	107	184	23
Average	28070	13503	2260	31753	88	112	173	25
Std Dev	397	145	231	488	15	24	14	3
Rel Std Dev	1.4	1.1	10.2	1.5	16.6	21.3	8.1	12.7

Table X-14 (cont'd): Duplicate XRF analysis of sediment samples (ppm).

Sample	K	Ca	Mn	Fe	Cu	Zn	As	Sb
28	12360	77130	1510	32270	134	179	1304	126
	12460	80750	1190	33400	30	171	1254	75
	13050	73580	1410	32940	50	126	1222	51
Average	12623	77153	1370	32870	71	159	1260	84
Std Dev	373	3585	164	568	55	29	41	38
Rel Std Dev	3.0	4.6	11.9	1.7	77.4	18.0	3.3	45.6
32	16600	67440	1910	66990	274	312	3292	313
	16030	67790	1640	65500	292	301	3324	362
	15960	68150	1870	68440	275	346	3321	343
Average	16197	67793	1807	66977	280	320	3312	339
Std Dev	351	355	146	1470	10	23	18	25
Rel Std Dev	2.2	0.5	8.1	2.2	3.6	7.3	0.5	7.3
34	20010	65600	1440	55550	151	432	2986	255
	20470	65620	1690	55620	183	424	3002	212
	19270	64730	1530	57610	172	379	3070	237
Average	19917	65317	1553	56260	169	412	3019	235
Std Dev	605	508	127	1170	16	29	45	22
Rel Std Dev	3.0	0.8	8.2	2.1	9.6	6.9	1.5	9.2
39	12210	68220	1890	72180	106	330	3351	367
	12290	68420	1550	71990	116	374	3371	348
	11480	62120	1500	61920	90	182	3744	276
Average	11993	66253	1647	68697	104	295	3489	330
Std Dev	446	3581	212	5870	13	101	221	48
Rel Std Dev	3.7	5.4	12.9	8.5	12.6	34.1	6.3	14.5
Avg Std Dev	566	1040	169	1257	25	35	59	29
Avg Rel Std Dev	2.9	2.0	12.1	2.3	16.2	13.2	2.7	16.2

A number of duplicates of leachate, surface water and porewater were analyzed. Samples were prepared in duplicate and analyzed (i.e. 1 vs. 2), and certain samples were analyzed twice (i.e. 1a vs. 1b).

Table X-15: Duplicate arsenic analysis of leachate, surface water and porewater (ppb).

Sample	1a	1b	2a	2b	Average	Std Dev	Rel Std Dev
Leachate							
4	2474	2486	2514	2294	2442	100.3	4.1
18	130		125		127	3.7	2.9
34	20	21	26	27	24	3.4	14.2
36	91		94	95	94	1.9	2.0
39	197		171		184	18.6	10.1
Surface Water							
3	2.9	2.3			2.6	0.4	15.4
4	63		58		61	3.6	5.9
4-4.3	2.1	2.2	2.7	2.5	2.4	0.3	11.6
9	1.3	1.2			1.3	0.0	1.9
9-4.5	1.3	1.5			1.4	0.2	11.9
9-9	1.3	1.3			1.3	0.0	1.8
20	101		103		102	1.3	1.3
21-0	2.0	1.9	1.5	1.3	1.7	0.3	19.0
21-5	2.8	3.0			2.9	0.2	5.4
21-11	1.1	0.8	0.9	0.7	0.9	0.2	22.5
22	77	68			73	6.4	8.9
25-11	11		12		11	0.5	4.1
Porewater							
2-5	78	76			77	1.0	1.3
2-10	35	31			33	2.3	7.1
4-0	1616		1700	1608	1642	51.2	3.1
4-5	3396	3346			3371	35.1	1.0
9-0	59	57			58	1.4	2.5
9-5	151	167			159	11.3	7.1
9-10	202	213			207	8.1	3.9
9-15	147	144			146	2.3	1.6
20-0	1323	1349	1309	1365	1336	25.3	1.9
20-5	579	494	458	484	504	52.2	10.4
20-10	760	748	738	774	755	15.6	2.1
21-0	834	760	780	800	793	31.7	4.0
21-5	1733	1706	1694	1702	1709	16.5	1.0
22-0	1451	1254	1413	1423	1385	88.9	6.4
22-10	1696	1825			1761	91.0	5.2
					Average	**18.0**	**6.3**