Northern Hard Rock Mining: Effects on Riparian Zones and Passive Biological Treatment of Impacted Waters

Prepared for:
West Kitikmeot Slave Society

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January 12, 2006

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January 12, 2006

Table of Contents

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List of Figures

List of Tables

List of Photographs

1.0 Background: Water Quality and Treatment With Respect to Hard Rock Mining in the NWT

As a result of previous hard rock mining, the insolvency of select mining companies and historically inadequate regulations[1], Indian and Northern Affairs Canada (INAC) is currently the steward of 63 properties known to contain contamination; liabilities stemming from ownership are estimated to be $754 million (Canadian dollars) (CSP 2003). In addition, current (i.e., producing diamond mines) and future hard rock mining developments and many additional mines in the exploratory and permitting process, pose a risk to the state of the pristine Northern environment, if not managed properly.

One common environmental liability that historical, current and future hard rock mines and their related stakeholders must all consider is the need to treat waters impacted from mine development and/or production. Water quality can be impacted by a variety of constituents (i.e., metals, nutrients, physicals, magor ions, process chemicals such as flocculants, cyanide and pH adjusting reagents etc.), resulting from a wide range of mining related activities. For example:

- *exploration for minerals:*
  -exploration requires camps, which produce waste such as grey/black water and employ hazardous goods such as petroleum products. These substances can find their way into the water table and/or surrounding water bodies; and
  -bulk sampling and other exploratory related disturbances expose mineral deposits to the elements, creating the potential for the leaching of metals from these deposits.
- *the extraction of ore:*
  -sulphide rich minerals can become exposed within open pits or underground mines, leading to the possibility of acid mine drainage;
  -ANFO explosives (an ammonia based explosive compound) leave behind residual concentrations of ammonia, which can seep into the environment from adit discharge, waste rock pile seeps etc.; and
  -underground mines must be continuously dewatered as ground water is constantly seeping into the workings (i.e., depressed water table). Depending upon the depth of the mine workings groundwater can take the form of brine (water typical of deep crystalline environments) (Intera 1997) . Brine contains high concentrations of salts (i.e., chloride and sodium) and mixes with the natural meteoric waters seeping in from higher levels or the surface. Eventually the brine must be stored above ground (usually along with tailings). As a result, salts present in tailings water may have to be removed prior to discharge from a tailings impoundment.

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[1] For example, environmental bonding to ensure funds for post closure remediation was not historically required by the government during the operational period of the legacy mines in the NWT.

- *the communication of ore:*

  -grinding of the mined ore leads to smaller diameter particles and therefore greater surface area and potential for mass transfer of elements to the aqueous phase.
- *the milling of ore*:

  -water is used as a medium to facilitate/enhance chemical reactions or aid in physical processes during the extraction of precious commodities. Chemicals are added to and metals dissolve into the aqueous phase. These chemicals and metals generally end up as dissolved constituents of tailings pond water. For example cyanide and cyanide compounds/breakdown products (i.e., metal cyanide complexes and thiocyanate) are present in the waste streams of gold mines employing the cyanidation process.
- *mining Infrastructure:*

  -functioning mines require vast amounts of infrastructure. Laydown pads, roads etc. are commonly constructed using waste rock, which can eventually leach metals;

  -grey/black water generated from mining personal requires treatment and storage and can potentially leach or be spilled into the environment; and

  -many fuels (diesel/gas) and other petroleum based products are commonly stored on-site in large quantities and can enter the environment incrementally through small spills or through events such as the failure of storage tanks.
- *storage of milling tailings:*

  -precious commodities are present in very small concentrations within the ore. The remaining bulk of the communicated ore is generally stored on-site within tailings containment facilities. Tailings containment facilities, in Northern Canada, are usually constructed by daming existing water bodies and subsequently filling the enclosure with the tailings product. The dams invariably seep and can leak or fail, possibly impacting the surrounding pristine water bodies. For example, Dam 1.0 at the Colomac Mine regularly seeps (Photograph 2) and Dam 11.0 at the Giant mine failed in the 70's releasing tailings into the Yellowknife river (Photograph 1).s
- *transportation of materials:*

  -hard rock mines must continually be re supplied with a wide range of products. In the North, the majority of supplies are transported over a vast network of ice roads. Trucks can break through the ice, leaking petroleum products and possibly toxic contents.

Table 1 lists specific examples of waters impacted by hard rock mining in the North.

There are many technologies available for treating waters impacted by hard rock mining in the North. An excellent review of these technologies, within the context of Northern treatment, was issued by INAC under the Northern Water Resource Studies Series of Documents. The reader is referred to this document, which is titled *"Applicable Technologies for the Management of Mining Effluents in the Northwest Territories"* (SENES 2002), for a complete review of Northern water treatment.

The specific form of water treatment technology which is chosen to mitigate water impacted by mining in the North is both an economical and performance based decision. In addition, the concentration of deleterious substances within and the quaintly of water to treat also influence technology selection. (i.e., a large concentrated point source discharge from a mill versus a small non point source and relatively dilute seep from an open cut). However, treatment methods must be invariably meet discharge criteria within budgetary constraints. In the North, most specifically at abandoned legacy mines, this can be a very challenging undertaking.

Northern mining properties are mostly situated in remote locations, which greatly increases the costs associated with the transportation of water treatment infrastructure and chemicals (i.e., air or winter road access). In addition, a much larger pristine environmental footprint is exposed to a spill event due to increased transportation distances across undisturbed lands. Furthermore, all materials and reagents must be procured and transported during a narrow time period when the winter roads are operational, leading to logistical difficulties.

In the case of abandoned Northern mines water treatment becomes even more challenging. Historical legacy mines generally have long term water treatment requirements. For example, tailings were commonly deposited, prior to the 1970's and the onset of environmental legislation, unmanaged into natural drainage basins (i.e., Con and Discovery). These forms of tailings deposits are spread over large footprints and are situated in topographical areas where surface water naturally flow overland (the liquid tailings followed natural water flow paths subsequent to deposition (Photograph 3) have the potential to leach metals for a long period of time. Discharge of metal impacted waters from these forms of tailings deposits have been noted over 60 years following deposition.[2] This drainage must be collected and treated prior to discharge. In addition, many abandoned sites do not have regularly constructed winter roads and do not require staffing for operations other than remedial activities. As such, servicing and operating a fully functioning conventional water treatment facility to treat chronic water quality issues becomes very expensive. Following magor decommissioning, no other activities justify the required infrastructure development (i.e., winter roads, housing of staff etc.) and costs are not offset from the sales of mining products.

As stated previously the selection of water treatment technology depends not only on economics, but also on the ability of the technology to regularly meet discharge criteria. Water quality criteria pertaining to the NWT can be divided into national and local and further into guidelines and legally binding limits.

On December 6, 2002, the Metal Mining and Effluent Regulations (MMER) came into force under the authorization of the Fisheries Act. The MMER criteria must be met by metal mine operating within Canada (historical mines and abandoned mines must apply for exemption). Like most other regulations, the MMER imposes prescribed discharge limits (cyanide, metals and suspended solids). However, the MMER further states that no effluent discharged from a metal mine can be acutely lethal to rainbow trout and the

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[2] Lower Pud tailings at the Con Mine.

water flea *Daphnia magna*. Environmental Effect Monitoring (EEM) is also required under the MMER, which aids in monitoring the effects of discharged water following dilution within the receiving environment (i.e., end of pipe discharge toxicity versus the toxicity of the discharge subsequent to entering the receiving environment). One important requirement of the EEM of the MMER is sub lethal toxicity testing with fathead minnows, the water flea *Ceriodaphnia dubia,* the alga *Selenastrum capricornatum* and the aquatic plant *Lemna minor.* These additional criteria shift the focus from treating select lists of deleterious substances to more robust water treatment technologies or treatment trains capable of removing a wide range of potentially toxic substances. For example, effluent from a gold mine located within the NWT has failed to meet the acutely lethal criteria of the MMER, despite employing conventional chemical water treatment methods which routinely met the criteria for removal of specific substances such as arsenic, copper and cyanide to legal discharge limits[3]. Treated discharge has regularly been acutely toxic to both the rainbow trout and the water flea *Daphnia magna* (EVS 2003). Rainbow trout toxicity was attributed to elevated ammonia levels (resulting from the breakdown of cyanide) and water flea toxicity was correlated to high concentrations of salts (inputs from deep brine water during dewatering of the underground workings).

The Canadian Council of Ministers of the Environment, Canadian Water Quality Guidelines for the Protection of Aquatic Life (CCME FAQG) are guidelines intended to protect freshwater life from anthropogenic stressors such as chemical inputs or changes to physical components (i.e., pH temperature and debris). The guidelines consist of numerically based limits or qualitative statements based on scientifically defensible toxicological data (CEQG 2002). The CCME FAQG are nationally set guidelines, which provide a benchmark for consistent environmental assessment. However, unless specifically adopted by provinces or other bodies with regulatory powers, the guidelines are not legally binding. The CCME FAQG have limits which are generally lower than the MMER limits as they are meant to be reflective of conditions in magor waters following the discharge of treated effluent. Furthermore, since the CCME guidelines are most applicable to large receiving bodies of water where aquatic wildlife are expected to reside, the application of the these guidelines to water such as small seeps from waste rock piles prior to entering the receiving environment may not be appropriate (in this case the MMER guidelines may be more applicable).

In the NWT, water quality is protected at the regional level through resource co-management boards adopted under various land claims legislation (Mackenzie Valley Resource Management Act). For example, the Mackenzie Valley Land and Water Board (MVLWB), the Gwich'in, and the Sahtu water boards all issue water licenses within their respective jurisdictions. One function of these water licenses is to set limits on the concentrations of various deleterious substances permitted in water discharged as the result of various activities related to development.

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[3] Precipitation of arsenic and copper with ferric iron and oxidation of cyanide with Hydrogen Peroxide.

Table 2 compares discharge criteria for key substance established by the MMER, CCME FAQG and the MVLWB.

Finally, the concentration and quantity of water requiring treatment also determines the technology that is selected to treat waters impacted by Northern hard rock mining. For example, a concentrated waste stream discharging from an operating mine could require a differing water treatment strategy than the treatment of non point source seepage from waste rock piles or historical tailings deposits.

Best Available Technology For Treating Arsenic Impacted Water in the North

Photograph 1 Flow path of tailings from historical tailings breach in the 1970's

Photograph 2 Dr. Sue Baldwin of UBC samplings seepage from Dam 1.0

Photograph 3 Unimpeded Historical Tailings Discharge into a Natural Drainage Pathway; Tailings prior to capping Gold Mine in the NWT)

Table 1 Water Impacted by Hard Rock Mining in the North

Mine Site	***Type of Impacted Water***	***Metals of Concern***	***Additional Elevated Water Quality Parameters***	***Information Source***
Giant/Supercrest Mine	Tailings Dam Seepage			
	Tailings Ponds			
	Mine Water			
	Open Pit Surface Water			
Con/Rycon Mine	Tailings Dam			
	Mine Water	As, Cu	Conductivity, TDS	
	Drainage from Historical Tailings			
Colomac Mine	Tailings Dam Seepage		Conductivity	
	Tailings Pond			
Terra Mine	Tailings Pond	As, Cu, Al, Cd, Cr, Fe, Pb	TDS,	1
	Tailings Pore Water	As, Al, Cd, Cr, Fe, Hg, Mo, Se, Ag, Cu, Pb, Ni, Zn	TDS, Conductivity, Magor Ions	1
	Mine Adits	As, Cu	TDS, Magor Ions	1
Norex	Mine Adits	Al, As, Cu, Fe, Pb, Zn	TDS, Conductivity, Magor Ions, Ammonia	1
	Waste Rock Seepage	Al, As, Cd, Cr, Cu, Fe, Pb, Ag, Zn, Mn, U	TDS, Conductivity, Magor Ions, TEH	1
Graham Vein	Tailings Pond	Al. As, Cu, Pb, Zn		1
	Open Cut	As, Cu, Pb, Zn		1
Northrim	Tailings Pond	As, Co, Pb		1
	Landfill Discharge[4]	Al, As, Cu, Fe, Pb, Zn, Co, Mn		1
	Adit	As, Al, Fe, Cu, Pb, Zn		1

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[4] Fuel Drums and old mining equipment, waste rock in general area and possible buried tailings

1. Silver Bear Mines Water Quality Monitoring Program (Rescan March 2005)
2.

Table 2 A comparison of discharge criteria for the MMER, CCME FAQG and the MVLWB water licenses

	Regulation/Guideline			
Constituent	MMER[1]	CCME CSQG	MVLWB Water Licence N1L2-0040[1]	MVLWB Water Licence N1L2-0043[1]
As				
Cu				
Pb				
Ni				
Zn				
Cyanide				

[1] Based on maximum grab sample

2.0 Current Best Available Technology for Treatment of Arsenic Impacted Water in the NWT

3.0 Metal Mobility, Transformations and Toxicity: Current Scientific Knowledge and its Relation to the North

Water quality and mine reclamation reports were reviewed for the following mine sites: Giant, Colomac, Tundra and Terra (1, 40). Most reports presented water quality data for tailings containment areas, mine pit lakes, waste rock tailings seepage and impacted lakes. Only one of the reports contained data from water quality monitoring of wetland areas, namely Colomac.

A review of data from the above mentioned reports, and additional reports pertaining to water quality, suggests that the following metals are of concern due to their concentrations being elevated above Canadian Council of Ministers of the Environment Freshwater Aquatic Guidelines (CCME FAQG): arsenic (As), copper (Cu), molybdenum (Mo), chromium (Cr), nickel (Ni), zinc (Zn), and lead (Pb). Of these, arsenic is the most worrisome due to its presence, within the majority of impacted waters, at concentrations very much elevated above the Guidelines and due to its extreme toxicity. In addition, the behavior of As in the environment is different than that of the other metals in many aspects. Thus, a more detailed summary of As in the environment will be discussed below. In addition, the following review includes information on the mobility, transformation and toxicity of the above listed metals in the environment with particular reference to the conditions at mines in the NWT. For each metal a summary of (i) environmental factors affecting the species present, their solubility, mobility, and toxicity and (ii) the major chemical and biochemical factors that transform metal species from one form to another, will be presented.

3.1 Arsenic

Arsenic is one of the metals of major concern in the environment within the NWT because of its toxicity at low concentrations and widespread occurrence at hardrock mining sites (i.e., refractory gold is contained primarily within arsenopyrite). The CCME FAQG recommend that arsenic concentrations be maintained below 5 $\mu g\ l^{-1}$ for protection of aquatic life. Because of the major concerns with arsenic in the environment there are many books and review articles written on speciation, mobility, transformation and toxicity of arsenic that were part of this literature review: (2, 3, 6, 11, 17, 27-29, 31, 32). Information from these sources was condensed and is summarized below.

Arsenic has four oxidation states, -3, 0, +3 and +5, however in aqueous solutions it is present predominantly as As^{3+} or As^{5+}. Its presence at mine sites in the NWT is mostly due to oxidation of arsenopyrite (FeAsS) during processing of refractory gold ores through the release of arsenic trioxide (As_2O_3) from roasting (i.e., Giant and Con Mine roasters: high temperatures and mildly reducing conditions) or from leaching of waste rock and/or tailings deposits. Arsenite (As^{3+}) is the more soluble and biologically toxic form of As, which exists under mildly reducing conditions. Arsenate (As^{5+}) is the less mobile form of As, which is believed to be the most prevalent form in aqueous environments of the Giant Mine area (Golder Report).

pE versus pH diagrams are most instructive for revealing which species are more thermodynamically stable depending on reduction potential and pH. The pE-pH diagram for As is replicated in Figure 1. At moderate or high electropotential (pE) or under oxidizing conditions, the oxyanion arsenate species, H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} are present. Under mildly reducing conditions, arsenite predominates. In mine tailing and sediment pore water where the conditions are mildly reducing, arsenite is the most likely oxidation state for As. Under very reducing conditions, such as are found in areas of high anaerobic bacterial activity, and in the presence of sulfides there is the potential for formation of arsenic sulfide minerals (most likely orpiment (As_2S_3)).

Arsenic mobility is affected by its ability to adsorb onto mineral phases and complex with organic compounds. In high pH environments, since As exists as negatively charged oxyanions, it is less likely to bind to hydrous oxide mineral surfaces and thus As is more mobile. For example, below pH of ~8-9 most arsenate was found bound to ferric oxide[5]. At pHs above this arsenate was released into solution (41).

The reduced form of As, H_3AsO_3, is more mobile that the oxidized form, $H_2AsO_4^{2-}$. Thus, the most mobile forms of arsenic exist at low pE and high pH: (i.e in mildly reducing alkaline environments). Thus, arsenic mobility will vary with depth in the mine tailings or sediment: first increasing and then decreasing with depth. For example, in a tailing impoundment at the Campbell Gold Mine, arsenic concentrations were low (< 1.5 mg l^{-1}) in the top 4.5 m, increased to a maximum (107 mg l^{-1}) at 5.2 m and decreased to less than 0.5 mg l^{-1} below 5.2m.

However, the nature of the soil or sediment can also influence As mobility. Soils and sediments with a high Fe, Al or Mn oxide and hydroxide content adsorb and immobilize arsenic species, particularly arsenate but less so arsenite. Iron oxyhydroxides in sediments are responsible for much of the immobilization of As. However, under reducing conditions, these iron oxyhydroxides dissolve liberating As back into the water. Similarly, high clay content soils render arsenic less soluble. Chemical oxidants such as ferric oxide and manganese oxide, if present in the sediment, can oxidize arsenite to arsenate. Materials with the highest amounts of citrate-dithionate extractable iron and percentage clay have the highest adsorption affinity for arsenate and arsenite at acidic pHs. At higher pHs, carbonates adsorb arsenate and arsenite. Adsorption of arsenate to soils and sediments is affected by the presence of competing anions, particularly phosphate ($H_2PO_4^-$), but also sulfate and carbonate.

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[5] A similar situation exists for the chemical treatment or As via precipitation with Iron. This process is employed at the Con and Giant Mine water treatment plants and requires the lowering of pH following the oxidation of arsenite to arsenate to approximately 8 pH units to allow the arsenate to bond to the oxyhydroxides in solution. s

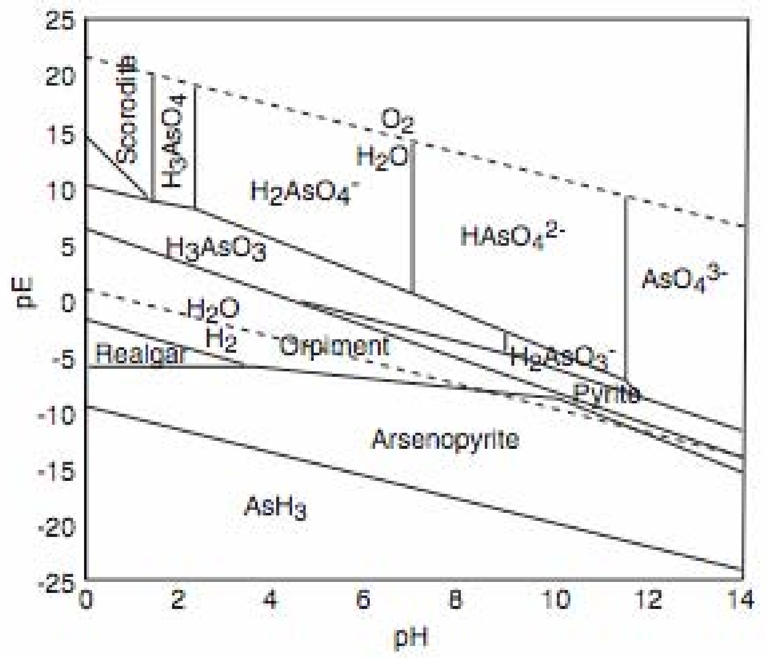

Figure 1: pE versus pH diagram for the As-S-H_2O system

In addition to the compounds in Figure 1, arsenic can exist in many other forms. Table 1 taken from Cullen et al. (8) shows those species found in freshwater and terrestrial environments. In addition to the inorganic species, arsenic is found in methylated and dimethylated forms, as arsine gas (AsH_3), arsenosugars plus many other organic forms. Some of these organic species, such as arsenobetaine ($(CH_3)_3As^+CH_2COO^-$), found in marine animals and mushrooms, are less toxic than inorganic As compounds. The general ranking of arsenic toxicity is as follows: (from most to least toxic): arsines > arsenites > arsenoxides > arsenates > pentavalent organic compounds > arsonium compounds > metallic arsenic.

Soil samples taken from within the Giant Mine site and from within the town of Yellowknife were analyzed for total As by Cullen et al. (8) as were samples of plants and animals. They found that mosses contained the most amounts of total arsenic (490-1220 mg kg^{-1}) and that *Typha latifolia* (cattail) takes up the least amount (0.52-5.0 mg kg^{-1}). *T. latifolia* is abundant at many wetland sites in the area and it is postulated that it may have an enhanced tolerance to As contamination. Terrestrial grasses and shrubs had between 3.6 and 84 mg kg^{-1} arsenic. Sedges (*Carex* sp.) had between 3.6 and 136 mg kg^{-1} and horsetails between 30 and 260 mg kg^{-1}. All of the terrestrial plants analyzed by Cullen et al. contained mostly inorganic arsenic forms. Thus, the availability of arsenic in these plants to animals that use them for grazing needs to be investigated. Some plants also contained much smaller amounts of methylated arsenic species.

Table 3 Additional Common Arsenic Species Found in Aqueous and Terrestrial Environments

As(III)	As(V)
$As(OH)_3$	H_3AsO_4 H_3AsO_3S
$CH_3As(OH)_2$ $(CH_3)_2AsOH$	$CH_3AsO(OH)_2$ $(CH_3)_2AsO(OH)$ $(CH_3)_4As^+$ $(CH_3)_3AsO$
AsH_3 CH_3AsH_2, $(CH_3)_2AsH$ $(CH_3)_3As$	$(CH_3)_3As^+CH_2COO^-$ $(CH_3)_3As^+CH_2CH_2OH$ arsenosugars
$As(C_2H_5)_3$ $CH_3As(C_2H_5)_2$ $(CH_3)_2AsC_2H_5$	$C_6H_5AsO(OH)_2$

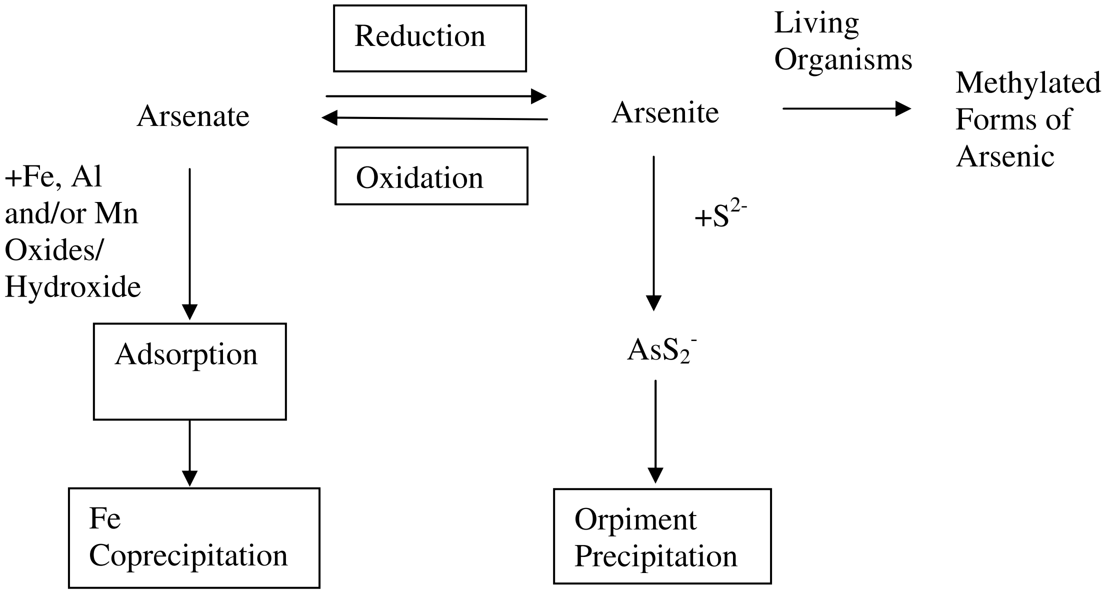

Figure 1 Chemical Transformations of Arsenic In Soils

The pE versus pH diagram presents the thermodynamically stable situation. However, the real environment is often dynamic and constantly in transition. Transformation of arsenic species can occur in wetland sediments and depends on the redox potential, the presence of oxidizing or reducing agents, microbial activity, precipitation, dissolution, adsorption and desorption. Arsenic can exert an influence on wetlands through its toxicity, which will result in growth of only arsenic resistant plants and bacteria. These organisms may have a beneficial effect if they are able to immobilize arsenic and prevent it from harming other life forms downstream.

Arsenate is an analog of phosphate and can enter the cell through phosphate transporters. Once inside the cell, arsenate can inhibit oxidative phosphorylation. The more toxic arsenite, uncharged at pH less than 9.2, enters the cell via aqua-glycerolporins. In the cell, it binds to sulfhydryl groups impairing the functions of proteins. Since As is found in many natural environments, living organisms have developed several defense mechanisms for de-toxifying arsenic for example through methylation and expulsion using an As-specific transporter. Many bacteria produce monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA). Fungi produce trimethylarsine and other animals and plants can convert arsenic to arsenobetaine and arsenosugars, which are much less toxic forms of arsenic. In marine environments, zooplankton and phytoplankton in the surface waters accumulate As and transport it to the bottom as biogenic debris.

As stated previously, arsenite is more toxic and soluble than arsenate. As such, microbial processes that oxidize arsenite will impact mobility, toxicity and speciation of arsenic. The ability of organisms to do this probably evolved as they developed ways of adapting to high As environments. More than 30 bacterial strains from at least 9 genera with As oxidizing ability have been reported (31). They can be broadly categorized into heterotrophic or chemolithoautotrophic oxidizers, HAO and CAOs, respectively. Heterotrophic oxidation occurs as a detoxification mechanism on the cell membrane to prevent As from entering the cell. CAOs couple arsenite oxidation to the reduction of oxygen or nitrate such that arsenite behaves as an electron donor. New arsenite oxidizing species have been isolated from As-rich thermal springs and lakes, such as Mono Lake[6], which have the potential to be used for bioremediation of systems impacted by As(III) (32).

In contrast, arsenate can be reduced to the more mobile arsenite through bacterial activity in anaerobic environments. A common detoxification mechanism carried out by many bacteria involves reduction of As(V) to As(III) by the ArsC system. Although As(III) is more toxic it can be excreted from the cell through an As(III)-specific transporter. Bacteria that can do this include *Clostridium sp.*, strict anaerobic heterotrophs, and *Desulfovibrio sp.*, sulfate-reducing bacteria (SRB). Such As reduction to arsenite and subsequent mobilization from sediments has been noted at mine-impacted sites. However, under highly reducing conditions in the presence of sulfate and SRB,

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[6] Mono Lake is a closed basin hyperalkaline (pH 9.8) and hypersaline (salinity = 90 g/L) lake in central eastern California. Arsenic concentration in the lake is 200 μM.

arsenite may combine with sulfide to form insoluble sulfides, such as orpiment, which is a mechanism for immobilization of arsenic. Sulfide is produced when sulfate is reduced by the SRB.

Furthermore, there are bacteria that use arsenate as an electron acceptor coupled with oxidation of a carbon source. These are called dissimilatory arsenate-reducing prokaryotes (DARPs). Two *Sulfurospirillum* species were the first organisms found to do this. Some SRB (*Desulfotomaculum* sp. and *Desulfovibrio* sp.) and selenate-reducing bacteria have the ability to respire on As as well as sulfate or selenate, respectively. DARPs have been found in many natural environments including gold mine sites, where their impact on As speciation and mobilization can be significant. Arsenic contaminated sediments have been found to contain $10^4 - 10^5$ cells per gram of bacteria. In mine tailing sediments, for example, DARPs can reduce arsenate (greater affinity for adsorption onto Fe and Al minerals, including scorodite) to arsenite (lesser affinity for absorption), thus mobilizing As into the water. This release of As from tailings or sediments has been observed at some mine sites.

A number of scientific studies have been performed on As cycling in natural and mine-impacted wetlands in temperate climates. La Force et al. (22) monitored As and Fe seasonally in a slightly acidic (pH = 5.7 – 6.7) wetland. Solid and aqueous phase seasonal As transformations were measured. Measurements carried out included X-ray absorption near-edge structure (XANES) for speciation and selective sequential extraction on the sediment and pore-water chemistry using peepers[7]. Arsenite, arsenic sulfides and arsenate species were present in the sediment. Pore-water As and Fe concentrations were highest in spring and summer. From the sequential extractions, As and Fe were positively correlated with the sodium acetate/acetic acid (carbonates), HCl (amorphous compounds), hydroxylamine-hydrochloride/acetic acid (crystalline oxide) and hydrofluoric acid (silicate) extractable fractions. Arsenite and arsenate species were associated with carbonates in the summer and iron hydroxides in the fall and winter, and silicates in the spring. In the solid portion: 22% of the As was as arsenite and 78% as arsenic sulfides (orpiment-like) (As partitions with sulfides in sediments). Seasonal changes in redox sensitive iron was found to influence the speciation and mobility of As. Temperature at the sediment-water interface increased from 7°C in the spring to 20°C in the summer resulting in increased bacterial iron reduction and release of As. Thus, changes in As and Fe correlated with one another. In the winter the wetland was chemically and biologically dormant and 85% of As existed as arsenate.

A study on a wetland receiving waste agricultural runoff revealed some interesting information about the effect of seasonal changes on metal release. Olivie-Lauquet et al. (30) maintain that dissolved organic carbon (DOC) is a major factor in determining whether metal retention or release occurs in wetlands. Reducing conditions and organic matter degradation are dependent on seasonal conditions such as temperature. Reduction of Fe and Mn oxy-hydroxides and organic matter in wetlands can result in release of metal contaminants. Metals complex with organic ligands (such as humic acids), which

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[7] Field apparatus for taking pore water samples.

can increase their solubility. Fe and Mn changed the most seasonally: In winter their water concentrations were low, increasing from Feb till May in phase with a marked decrease in reduction potential (Eh) (from 400 to 250 mV), which was probably due to increased microbial activity with increasing temperature. Fe and Mn concentrations markedly declined in May for reasons not given. Arsenic concentrations increased in phase with Fe and Mn increases. In these waters sulfate concentration was very low and thus no sulfide precipitates formed. Metal release was in phase with temperature increase (5 – 12°C), redox decrease and DOC increase (10 – 30 mg/L). At the end of the study period, DOC and all metal concentrations decreased. The authors hypothesized that this was due to microbial activity depleting DOC levels in the water, but further information would be required to substantiate this claim.

Fox et al. (12) investigated constructed wetlands for remediation of metal contaminated agricultural water in the San Joaguin valley. At the sediment-water interface, As was released into the water due to the mildly reducing conditions. Reduction potential was lowest in the top 2 cm of the sediment due to high DOC and microbial activity, and increased with depth due to high pH, low salt concentrations and low nutrients. In the highly reducing layer (top 2 cm of the sediment) As accumulation occurred. However, pore water As concentrations increased with depth in the sediment due to mildly reducing conditions below the top 2 cm highly-reducing layer. Arsenic was evenly distributed in the extractable fractions.

Thus, As speciation in mine tailings, impacted lakes and ponds is complex and depends on the chemistry and microbiology of the water column and sediments. Factors that promote arsenite oxidation to arsenate, chemical or biological, will render As less mobile and toxic. Arsenic taken up by plants and animals may be converted into organic forms, some of which may be less harmful. However, organisms that reduce arsenate, either for respiration or detoxification, result in mobilization of As into the water. These organisms favor a reducing environment such as might exist in the top layers of the submerged sediment surface. Also, iron reducing bacteria render iron more soluble liberating As into the water.

That being said, there is strong evidence that, under more reducing environments where sulfate and SRB are present, As can precipitate as arsenic sulfides (orpiment-like or sulfide co-precipitates with Fe and Zn), which are sparingly soluble as long as the sediments are not re-oxidized. This represents a sink for arsenic since such precipitates would immobilize As in the sediments. Formation of arsenic sulfide precipitates depends also on the pH and may not occur in alkaline waters. The formation of arsenic sulfide precipitates in reducing, anaerobic environments where SRB are active is an As removal mechanism that can be exploited in anaerobic treatment systems. Several of these are being used for As contaminated mine water treatment and will be reviewed later.

To summarize, the effect of environmental parameters on the mobility of As are arranged in two columns in Table 2. The left hand side column lists factors contributing to immobilization of As and the right hand side column lists those contributing to release of As into aqueous systems.

Table 4 Summary of the Main Environmental Processes Affecting Arsenic Mobility

Arsenic Immobilization	Arsenic Mobilization/Release
Oxidation to arsenate	Microbial reduction to arsenite under reducing conditions
Co-precipitation with iron in oxic zones	Reducing environments (due to dissolution of Fe and Al oxyhydroxides)
Co-precipitation with sulfide in anoxic zones	Mixing of sediments due to disturbance, wind or burrowing animals.
Adsorption to Fe, Al and Mn oxides and clays	Increased temperatures (late summer – early fall)
Conversion to some organic forms	Very acidic environments
Adsorption onto solid organic ligands	Very alkaline environments
	Phosphate concentrations (competes with arsenate for absorption)

3.2 Missing information on As speciation, mobility and transformation in mine-affected wetlands of the NWT

Arsenic concentrations throughout the Giant Mine area have been thoroughly documented and some As speciation ((As(III) or As(IV)) determined in surface water and Baker Creek sediment. Total As concentrations in soils (8) and As concentrations and speciation in plants have been determined (21)(reviewed earlier) at the site. The highest As concentrations in soil are found in the mine mill area (up to 87,000 mg kg^{-1}). The water soluble As in these soils was between 0.3 and 58% with an average of 13%. It is hypothesized that this soluble As phase is composed of calcine associated As and As_2O_3 dust (Golder Report). Within the soils surrounding the mill area, CCME exceedences were found for metals: Cr, Cu, Va, Ni and Zn. Just north of the mill, there is a Baker Creek wetland where As concentrations of 2,838 and 3,824 mg kg^{-1} were measured within sediments (8). Water soluble As in Baker Creek sediments varied from 0.12 – 0.25%, lower than that found in soils. Cd, Cr, Cu, Pb, Ni and Zn concentrations in Baker Creek sediment were all higher than CCME guidelines. South of the mill there are some marshy areas for which no data was found. It is not known what speciation of arsenic is in the sediments of these ponds and Baker Creek nor whether release of As and metals from the sediments will continue after mine closure. AEL and UBC sampled these two wetlands in our August 2005 field trip as described elsewhere.

Tailing material from the Giant Mine has been characterized as fine-grained (generally < 50 μm) containing quartz (SiO_2) and carbonate minerals ($CaCO_3$, $CaMg(CO_3)_2$, $KAl_3Si_3O_{20}(OH)_2$) some sulfides (including arsenopyrite) and roaster products (calcine containing hematite). Arsenic concentrations in the tailings are in the range 2,000 – 4,000 mg kg^{-1}. Only 0.2% is assumed to be water-soluble. Soluble As was previously hypothesized to exist associated with calcine adsorbed onto hematite particles (Golder Report). The stability of the other forms of As in the tailings and the potential for As release over time from leaching of the tailings is not known. Tailing pore water contained high sulfate, chloride, total suspended solids, low dissolved oxygen (<0.5 mg l^{-1}) and an As concentration of 4.4 mg l^{-1}, mainly as arsenate. Arsenic contaminated water and tailings have been discharged into wetlands and Baker Creek, but it is not known what the fate of As is in these systems. In addition, a historical breach of Dam 11 on the North Tailing Pond resulted in a substantial spill of tailing material down a flow path towards Yellowknife Bay. Several catch ponds and natural wetlands exist along this path. Water quality and sediment sampling has shown that these ponds downstream of Dam 11 have been impacted by the mine (Golder Report: Appendix A-1). Arsenic concentrations in these ponds were higher nearer the Dam, but it is not known if the As originates from the spilt tailings or from leach water seeping out from the tailings pond. No data for As speciation, mobility and transformation exits for these wetlands. And it is not known if the sediments in these wetland areas and Baker Creek will be a source for metals after mine closure. Thus the following missing information is required to assess these systems as future sources or sinks for As.

- The vertical distribution of arsenic species in the water and sediment of wetlands adjacent to the mine site needs to be determined as this strongly influences the mobility and toxicity of As. Little is known about the formation of organic As species in freshwater environments. Microalgae and zooplankton in terrestrial waters have the ability to methylate As. At other As contaminated sites in the temperate climates, methylated forms have been found in sediments.
- Forms of As present in the sediments should be determined using sequential extraction to identify which fractions As is associated with, which will help to determine the likelihood of As re-release.
- The vertical profile of other chemical compounds such as nitrate, phosphate and sulfate in the pore water need to be determined as these influence As transformation. For example, nitrate inhibits As reduction and phosphate competes with arsenate for adsorption sites.
- Microbiological community analysis should be done on the sediment to determine (i) the impact of As on total bacterial populations and (ii) the presence of As oxidizing or reducing organisms, particularly sulfate-reducing bacteria. Sulfate-reducing bacteria have the potential to promote formation of arsenic sulfide precipitates (e.g. orpiment), which is a potential sink for As in the sediments.
- Time course experiments need to be carried out so as to predict the net As release from or uptake to the sediments.

3.3 Other metals of Concern at NWT Hard Rock Mining Sites

Although arsenic is the metal contaminant of most concern at abandoned mines in the NWT, due to its prevalence at concentrations well above recommended guidelines and its extreme toxicity, there are other metals of concern. These have been found to be above background concentrations in impacted wetlands and lakes. A brief review of the forms likely present in aquatic systems of the North based on a review of their pE versus pH diagrams is presented below. Brief information is also given on their toxicity and factors influencing their mobility, summarized from reviews in the literature (16, 33-36).

3.3.1 COPPER

Copper has three oxidation states, (I), (II) and (III), of which (II) is the normal oxidation state for aqueous environments. It is very toxic at relatively low concentrations to fish, invertebrates and amphibians, and bioconcentrates in some fish and mollusca. Only a moderate amount of Cu accumulates in plants. Mammals are not as susceptible to Cu toxicity as are aquatic organisms, although they do suffer a wide range of effects.

Copper is more mobile in acidic environments at pHs less than 6.0, above which it forms stable precipitates. For example, in the presence of sulfide and under reducing conditions, covellite (CuS) and chalcocite (Cu_2S) form. Copper strongly adsorbs to organic matter, clays and carbonates. Thus, copper can be removed from the aqueous environment through adsorption and precipitation as relatively insoluble ($\log K_{sp} = -36$) sulfides in $pH > 6.0$ within reducing environments.

Because of the sensitivity of the aquatic environment to copper, this metal is of concern at several Northern mine sites especially those with potentially acid generating waste.

3.3.2 MANGANESE

Manganese exists in a number of oxidation states ranging from (-III) to (VII). Of these, the (II), (III) and (IV) states are of primary importance in a geochemical context. Some effects of Mn toxicity have been observed in birds. The soluble and mobile form is Mn(II), which exists under mildly reducing conditions. The oxidized form, Mn(III), is relatively insoluble. Manganese oxides are produced by microorganisms and are important for metal adsorption. However, manganese like Fe is mobilized under mildly reducing conditions resulting in release of bound metals into the aqueous environment.

3.3.3 NICKEL

Nickel is stable as Ni^{2+} over a wide range of redox potentials and at $pH < 6.5$ in aquatic environments. Its toxic effects include tissue damage, genotoxicity, and growth reduction. Mollusca and crustacea are particularly susceptible. Nickel will form insoluble hydroxides at pH above 6.5. Also, like other divalent cations it adsorbs onto iron and manganese oxides, or forms complexes with inorganic ligands (OH^-, SO_4^{2-}, Cl^-, or NH_3). Like Cu, Ni will be mobilized at acid generating sites. Also like Cu, immobilization of Ni in the sediment depends on the surface-ligands present and the number of available adsorption sites.

3.3.4 CHROMIUM

This element is found commonly in two oxidation states: (III) and (VI), which have very different chemical properties and biological effects on living organisms. Cr(VI) exists as an anion, it is more readily liberated from soil and sediment particles, and is considered the more toxic form. Chromate (CrO_4^{2-}) is in pH-dependent equilibrium with other forms of Cr(VI) such as $HCrO_4^-$ and dichromate ($Cr_2O_7^{2-}$), with CrO_4^{2-} the predominant form at pH > 6. Cr(III) is much less mobile and adsorbs to particulates more strongly. The solubility of Cr(III) decreases above pH 4 and above pH 5.5 complete precipitation occurs. Chromium (VI) is the more stable form in equilibrium with atmospheric oxygen. However, with its high positive reduction potential, Cr(VI) is a strongly oxidizing species, and in the presence of soil organic matter is reduced to Cr(III). Reduction is more rapid in acid than alkaline soils, hence in most soils, the relatively insoluble and less mobile Cr(III) form predominates and it generally occurs as insoluble hydroxides and oxides.

3.3.5 LEAD

Two stable oxidation states are (II) and (IV), however, the dominant form in inorganic compounds is (II). Lead compounds are generally poorly soluble at pH above 5.0, except the nitrate, the chlorate, and to a much lesser degree, the chloride. Lead is a neurotoxic metal that bioaccumulates. It has no biological value and disrupts many enzyme systems dependent on other metal ions.

3.3.6 ZINC

The dominant oxidation state of zinc is Zn^{2+} when pH is below 7.7. When the soil is more alkaline (pH > 7.7), minerals of zinc such as $ZnOH^+$ are more prevalent. The solubility of zinc increases with decreasing pH. As with other metals, like Cu and Ni, the mobility of zinc in soil depends on a combination of dissolution-precipitation reactions as well as adsorption-desorption and complexation processes. Since waters in the North are circum-neutral zinc will likely be in the more mobile aqueous form, Zn^{2+}.

4.0 Passive Biological Treatment of Arsenic contaminated Waters

Given that metal concentrations are above the recommended guidelines within impacted waters at many hard rock mine sites in the Northern Territories, there is a need to mitigate their impact on the environment. Seeps from tailing containment areas and waste rock piles are a route for introducing metals into pristine aquatic systems. AEL and UBC performed a literature review to ascertain the appropriateness and applicability of passive treatment systems, such as engineered and constructed wetlands or anaerobic bioreactors, for removal of the metals of concern from seepage streams before they enter the receiving environment. There is ample evidence that, if properly constructed and maintained, these can be low-cost, effective, long-term solutions to metal pollution at some sites. Although, not commonly applied in the North for removal of metals, there is some indication that passive treatment systems can function effectively at low temperatures. The following will be presented below: examples of successful metal mitigating wetlands, their general design principles and experience with their use and their applicability to the North. Also noted is key information, which is missing from the literature and proposed future work.

4.1 The Use of Constructed Wetlands for Mine Drainage Treatment

Engineered or constructed wetlands have been used for municipal wastewater treatment within Northern remote communities for many years where organic components and nutrients (N and P) in the feed water are removed through bacterial activity in the wetlands. Examples include the Rae, Edzo and Yellowknife water treatment facilities.

Starting twenty or so years ago, water quality was observed to increase after flowing through natural or volunteer wetlands at mine sites. This prompted the development of artificially constructed wetlands for mine drainage water treatment at many mine sites. In 1991, there were ~400 operating treatment wetlands at mines in the United States (26). Many of the first wetland mine treatment systems were developed for acid rock drainage from coal mines in the Eastern U.S. Several reviews and articles have been written on these (39 and the references therein).

Constructed wetlands have the advantage over natural wetlands that conditions conducive to sulfate-reducing bacteria (SRB), the organisms largely contributing to long-term sustained treatment of metal impacted waters, can be maintained. In addition, the hydraulic regime of the wetland system can be designed for optimal mass transfer conditions. The flow path of water through the wetland can be directed through the subsurface sediment layer, where SRB activity is the greatest. Longer residence times can be better maintained in a constructed wetland versus a natural wetland where short-circuiting could occur. Other advantages of wetlands over chemical treatment processes include: lower cost and maintenance requirements, improvement of the appearance of the mine site, and provision of habitat for flora and fauna.

In additional, engineering subsurface flow wetlands or anaerobic reactors can be constructed to minimize direct contact between the impacted water and wildlife, which can be a determining issue related to public perception and acceptance of passive wetland treatment systems. Subsurface flow methods can also be implemented for portions of the treatment train where concentrations of impacted waters are at their highest levels.

4.2 General Design Principles

In mine drainage treatment, the main goals are increase of pH, through sulfate reduction and neutralization, and metal removal. The chemical processes desired are the following:

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO^{3-} \qquad (1)$$
$$H_2S = HS^- + H^+ \qquad (2)$$
$$HS^- + Me^{2+} \rightarrow MeS_{(sink)}\downarrow + H^+ \qquad (3)$$

In the first equation, bacterial activity by SRB results in oxidation of carbon sources to carbonate and reduction of sulfate to sulfide. Depending on the pH, sulfide is present as H_2S or HS^- in aqueous systems. At a pH of 7, H_2S and HS^- are present in approximately equal amounts. Only at very high pH not encountered in natural systems does the species S^{2-} occur. Soluble sulfide combines with metal cations in solution, which, depending on the pH, precipitate as sparingly soluble metal sulfides. As long as these metal sulfides are not exposed to oxidizing conditions, they are effectively stabilized in the wetland sediment. For this treatment process to work, the wetland requires an adequate supply of carbon sources, through the degradation of organic matter, anaerobic conditions and sulfate.

Sulfate reduction rates in natural and constructed wetland systems vary with pH, temperature, C-source and nutrient availability, concentration of inhibiting compounds such as sulfide and competition from other bacterial groups. Optimal pH for SRB is in the range 6 – 9. Metal precipitation as sulfides depends on the pH. To remove almost all of the metals of concern, pHs greater than 9 are often required. Similarly, in chemical treatment systems, such as lime precipitation, high pH is also required for total metal removal.

The temperature dependence of sulfate reduction by SRB is given by:

$$k_T = k_{20}(1.09)^{T-20} \qquad (4)$$

At 4^{o}C the sulfate reduction rate is one quarter of the rate at room temperature (25^{o}C). Although kinetics increases with increasing temperature, so does competition from other bacterial species. Thus, highest sulfate reduction rates are often found in spring or at mild temperatures of 10 –15^{o}C.

Sulfate reducing bacteria prefer low molecular weight electron donors as carbon sources; fermentation byproducts such as lactate, ethanol, and propionate, for example. They can grow also autotrophically, that is by using CO_2 and H_2 as carbon and energy source, respectively However, in most cases, syntrophic relationships are required with bacteria that decompose organic matter and fermentative organisms that provide carbon sources for the SRB.

The usual limiting factor for sulfate reduction, if nutrients are amply supplied, is the build up of sulfide, which inhibits bacterial growth. Above concentrations of ~300 mg L^{-1} sulfide, sulfate reduction more or less stops. In mine treatment wetlands, only enough sulfate reduction is required to supply sulfide for metal precipitation. The build up of sulfide is usually not an issue as long as the system is not overloaded with nutrients. In addition, in natural systems, much of the sulfide produced by sulfate reduction does not accumulate as soluble sulfides, but is removed by co-precipitation with Fe, reacting with organic matter and through gas-exchange with the air (37).

As the redox potential decreases with depth in a wetland, the following sequence of electron acceptors is thermodynamically preferred: O_2, NO_3^-, MnO_2, $Fe(OH)_3$, SO_4^2 and CO_2 (methanogenesis). Thus, the presence of nitrate or iron hydroxides could inhibit sulfate reduction in favor of denitrification or iron reduction. Typical measured rates for sulfate reduction in natural and constructed wetland systems are in the range 0.4 – 3,000 nmol cm^{-3} day^{-1}. Required residence times are up to 15 days and depend on the wetland design. The suitable residence time needs to be carefully determined experimentally for each system so as to avoid washing out the bacteria.

When mine drainage enters a wetland, Fe and Al precipitate out first followed by other metals. Mechanisms other than precipitation exist for metal removal in a wetland, including: adsorption to inorganic oxy-hydroxides and organic matter, complexation with organic ligands and uptake by plants. Adsorption is responsible for ~50% of metal uptake (39), however, overtime, available sites for adsorption are expected to decrease without sufficient replenishment of organic material. Thus, precipitation as metal sulfides remains the mechanism most important for long term sustainable operation of the wetland. Although plant uptake is one route of metal removal, this may have undesired effects on animals grazing on the plants. *Typha latifolia* (cattails) are commonly used in wetlands since they are metal tolerant and do not hyperaccumuate metals. Depending on how fast they proliferate, they could provide some replenishment of organic material in the wetland, increasing bacterial activity and replenishing adsorption sites. Mosses, such as Sphagnum, have been used in some wetlands in the past since they hyperaccumulate some metals, as have algae. However these are no longer considered effective. The more important roles for plants in a wetland are: (i) for primary C production for microbial processes, (ii) to provide surface area for attachment of microorganisms and (iii) to provide O_2 in their root zone. The latter role is important for treating high organic loadings aerobically. In anaerobic wetlands, plants also provide a windbreak preventing O_2 transport from the surface into the sediment.

Engineered wetlands are typically constructed in stages (cells), with the first stage being a holding pond, followed by subsurface flow channels with or without plants (commonly cattails (*Typhia latifolia* if plants are employed), with a final equalization pond. Control of flow path is critical in engineered wetlands to maximize contact time of the water to be treated with the areas where SRB grow. Infuser pipes, dams or baffles that force the flow down through the sediment layer are incorporated into the design. Depths of these anaerobic treatment wetlands are typically 0.8 – 1.5 m, with a bottom layer of gravel on top of which a 40-50 cm layer of organic matrix is placed with a cap of 10 –20 cm water or soil. Many different types of organic material are used as substrate in the wetlands with varying degrees of success. One mixture that is often recommended includes 50% peat/compost/manure, 30% hay and 20% soil. In addition to providing nutrients, the organic matrix should have a high surface area and porosity to maximize exposure of water to biofilms.

4.3 Lessons Learned

Temperature is often cited as a limiting factor in the year-round application of wetlands. However, there are many reports of functioning wetlands with little reduction in treatment efficiency during the winter time when water temperatures are as low as 2 – 4^{o}C (13, 18, 20, 23, 25). Laboratory experiments have shown that SRB are still active at 4^{o}C although sulfate reduction rates are one quarter of those at 25^{o}C. Depending on the metal concentrations in the water to be treated, this may still be sufficient for metal removal.

Successful removal (> 99%) of metals such as Cu, Zn, Pb and Cd is often reported (5, 24, 38, 44, 45). Chromium exists as Cr(VI) in aqueous environments, has a high reducing power and thus is toxic and mutagenic. In wetlands, SRB have been found to reduce Cr(VI) to Cr(III), which is relatively insoluble and less toxic (7). Bacteria isolated from Cr contaminated environments have demonstrated the ability to remove 80 – 95% of Cr in concentrations ranging from 50 – 2000 mg L^{-1}. Nickel has also been observed to be removed in bench-scale compost bioreactors (15) and in actual wetlands (10). Enhancement of bacterial activity through lactic acid addition increased Ni removal. There are mixed reports of manganese removal in wetlands (19). Oxidation of Mn(II) to the less soluble Mn(IV) occurs only at pH above 8 and Mn does not readily form sulfide precipitates. Manganese and Fe are sometimes released from wetlands rather than removed (42). However, some studies did achieve Mn removal, or alternate bacterial treatments were shown to work (14, 44). Organic amendment of mine pit lake water with potato waste and steer manure resulted in increased SRB activity and removal of iron and arsenic (4).

Bacterial processes have been exploited to remediate cyanide contaminated mine sites. The best example of this is the natural attenuation of cyanides in Tailings Lake at Colomac mine through phosphate addition. At other mines, carbon amendments have resulted in increased bacterial degradation of CN (43).

4.4 Applicability to the North

A field survey conducted by AEL and UBC of the Colomac, Discovery and Giant Mine sites in August 2005 revealed many natural, volunteer and constructed (as drainage catch ponds) wetlands adjacent to and receiving seepage water from mine tailings dams and other mine contaminated sites (see the section describing the August field work). Past surveys of these wetlands revealed decreases in concentration of metals between inflow and outflow from these ponds. At the Colomac mine there are three wetland areas adjacent to Tailings Lake: Wetland A follows a flow path from Dam 1 to Paddle Lake, Wetland B flows North East from the top end of Tailings Lake and Wetland C follows a course through Cone Pond, to Heart Lake and discharges into Whaletail Bay. AEL and UBC visited only the first two wetlands in August 2005. The Colomac Remediation Plan report contains information on some parameters in these wetlands: (1). The pH is in the circum-neutral range, which is suitable for microbial processes such as sulfate-reduction. Conductivity in general decreased along a transect through Wetlands A and B. AEL and UBC found conductivity to very high (1,477 µS) at the seepage point from Dam 1 probably due to the high concentration of ions leaching from Tailings Lake. Phosphorus and ammonia concentrations were high (above the Guidelines) at the entrance to Wetland A, whereas nitrate concentrations were highest in the middle of the section probably due to nitrification of ammonia. Exiting nitrate concentrations were low. Thus, natural processes for uptake of these nutrients appear to be active within this wetland area. On the other hand, cyanide, arsenic, copper and molybdenum concentrations were all above the guidelines throughout Wetland A, which appears to be the most effected of the three as it is receiving direct seepage from the leaking Dam 1.0. Wetland areas surveyed by AEL and UBC close to the Dam 1 seepage, supported growth of *Typha* and other species. Thus, this area would most benefit from constructed wetlands. Clearly vegetation growth is supported in these waters and some natural attenuation of nutrients and metals is occurring. However, metal concentrations are still above the Guidelines. Often, natural wetlands are not effective at removing metals from very contaminated waters due to channeling of water through the wetland (reduced reaction rates due to reduced contact of impacted waters and biological processes) or insufficient supply of organic material. Thus, constructed wetlands with organic amendment and flow path design would be a more effective route for treatment than using existing wetlands in this area. Although, no bacterial activity will occur when the water and sediments are frozen during the winter, the area will clearly support bacterial activity during the summer months. Furthermore, during the peak treatment periods over the summer months in the North, sunlight is present during the majority of the day, leading to extended periods of treatment in comparison to Southern treatment locations (i.e., higher vegetation growth rates, consistent temperatures etc.). The water temperature in the polishing pond downstream of Dam 1 seepage was 10.8^{o}C at which significant bacterial activity will occur. Some other collection sumps around Tailings Lake were supporting growth of plants such as *Typha sp.* and contained a layer of sediment which AEL and UBC sampled.

4.5 Successful Case Studies

4.5.1 ARSENIC TREATMENT WETLAND IN TRAIL B.C.

A capped landfill adjacent to the operating Teck-Cominco lead-zinc smelter in Trail, B.C. contains toxic amounts of zinc, cadmium and arsenic, which are leaching into the watershed. A Canadian company called Nature Works Remediation Corporation began building and testing a constructed wetland system to treat this leachate in 1997. Their process consists of six cells: two anaerobic bioreactors followed by three horizontal sub-surface flow (HSSF) cells, and a pond wetland cell. The anaerobic bioreactors, where most of the treatment occurs, contain between 600 m^3 and 750 m^3 of substrate material, which is a mixture of 60% composted pulp and paper mill waste, 35% sand and 5% manure together with limestone gravel. The HSSF wetlands are vegetated with specific plants that are being tested for metal uptake.

The system treats 20,000 L day^{-1} containing 103 mg L^{-1} arsenic (average over the past two years) and spike events loaded with up to 500 mg L^{-1} As have been treated in the past. For their specific configuration, 98% treatment efficiency is achieved in a residence time of 3 – 5 days. This process has been operating continuously since 2002, including during the winter. Although the air temperatures at Trail in the winter can drop to –18°C, the ground water and influent temperature stabilizes at 4°C. Despite the slower sulfate reduction kinetics at this temperature, treatment effectiveness does not change between summer and winter. Sulfate reducing bacteria and iron reducing bacteria have been detected in the anaerobic bioreactors and it is thought that both filtration and precipitation as metal sulfides are the main mechanisms of removal.

4*.6 Challenges and Areas for Further Research.*

The main challenges and research needs are in long-term field monitoring of treatment wetlands to provide data for their design and control. More specific areas of missing data and research are given below (19).

- Wetland sizing is difficult due to the lack of reported field data for metal removal rates per surface area.
- There is a lack of long-term testing and data on actual treatment wetlands, especially the long-term evolution of microbial communities and changes in carbon source availability, although currently work in this subject is underway on this in the Department of Chemical and Biological Engineering at the University of British Columbia in Dr. Baldwin’s laboratory.
- Inadequate flow-path control and insufficient use of the whole surface area can lead to treatment failure.
- There are limited controlled studies on the actual benefit of plants to a treatment wetland. Plants impart both benefits (9) and detriments to the microbial community in a wetland and it is not always known what the net affect is.
- Futile cycling occurs in wetlands. Oxidation occurs in surface regions and reduction in subsurface zones resulting in recycling of some compounds like Fe and S. For example, sulfate reduction to sulfide occurs due to SRB in the sediments, and sulfide is re-oxidized to sulfate in the surface waters by sulfur-oxidizing bacteria (SOB). Net S removal could occur if metal sulfides are precipitated in the sediment. Whereas, on the other hand, S re-release may occur from sediments exposed to oxygen. Seasonal changes in water level may result in alteration between uptake and release, thus each system must be carefully designed and monitored so as to maintain consistent conditions.

5.0 Future Work

The AEL and UBC literature review focused specifically on metal mobility and transformations in wetland sediments and the potential for the use of engineered wetlands or anaerobic bioreactors for their removal. Following on from the literature review, AEL and UBC would like to propose research with the following objectives:

1. to determine the impact of mining on wetland sediments in the Northern Territories.
2. to determine if a constructed treatment wetland or anaerobic bioreactor can remove metals from mine tailings seepage water before it enters the pristine environment.

The first objective will be embarked upon in phase one commencing in May 2006 for four months. Phase one will provide “proof of concept” for passive removal of metals using native substrates collected from Northern hard rock mines during the summer field season.

5.1 Phase one (May – August 2006)

Samples were taken in August 2005 from natural or voluntary wetland areas at three mine sites in the NWT: Giant, Discovery and Colomac. These wetland areas were receiving or had been impacted by mine leachate or tailings material deposition. Water and sediment samples were transported back to the laboratory with the goal to determine how mining has affected the metal speciation and microbial communities in these wetland areas. To our knowledge no one else has investigated metal speciation and its relation to microbial communities in mine impacted wetlands in the North.

5.1.1 SCOPE OF FUTURE WORK

5.1.1.1 Metal Speciation in Sediments (UBC and AEL)

Little work has been done to date on metal speciation in sediments from these mine-impacted sites, although the transport and fate of metals in these wetland environments depends on the species present. We will carry out extraction experiments (sequential extraction) on sediment samples to remove sequentially water soluble, ionically bound, (oxy)hydroxide-, carbonate-, sulfide-, organic matter-associated and recalcitrant mineral forms using standard methods from the literature. This will reveal which fractions the metals of concern are associated with and therefore how mobile they are. From this data toxicity and stability of the metals can be inferred. In addition, the form of the soluble metal present in the extracts will determine the potential for treatment of leachate from sediments with similar properties.

5.1.1.2 Microbial Communities (UBC and AEL)

Here we will extract DNA from the sediment samples and perform quantitative polymerase chain reaction (q-PCR) experiments to see if populations of bacteria are present. We will use specific primers to measure the numbers of sulfate-reducing bacteria present. If our results are positive and show that SRB are already present in these environments, then there is the potential to use biological treatments that rely on SRB at these mine sites.

5.1.1.3 Northern Biological Substrate Survey (Nature Works and AEL)

One essential aspect of a passively based biological treatment system is a suitable source of carbon to be used as a substrate for biological growth within the bioreactor. As such, for Northern passive biological treatment of water impacted by hard rock mining to be successful a local carbon source will have to be located. To this end, Al Mattes and Jim Hall of Nature Works Remediation Corporation will travel to Yellowknife to conduct a survey of the available and suitable sources of carbon. This survey will be undertaken in early May. Some sources of carbon to be investigated are: biosolids, composting of on-site organic material grown by the treated water from the bioreactor (sustainable carbon source), pulpmill waste solids and wood chips. Samples of various Northern available carbon sources will be collected and shipped to UBC in preparation for the bench scale experimentation of the passive anaerobic removal of metals from mine impacted waters. In addition, the logistical difficulties of transporting off-site carbon sources to remote Northern hard rock mines will be investigated. It is proposed that at this point in time, water be collected from a impacted source in the North and shipped along with the carbons source to UBC for use in bench scale experiments (for example water could be collected from the Tundra Mine site).

5.1.1.4 Bench Scale Column Treatment Study (Nature Works, UBC and AEL)

The University of British Columbia, Department of Chemical and Biological Engineering (Dr. Sue Baldwin) and Nature Works Remediation Corporation (Al Mattes) will perform laboratory mesocosm experiments to assess the potential for metal uptake by these sediments. The previously collected carbon sources and wetland sediments (source of indigenous SRB) will be employed. In these experiments, we will expose, under anaerobic conditions, sediments taken from the field to both artificial mine seepage water and site specific impacted water from a Northern Mine. The change in metal concentrations over time will measured as the response variable. These experiments will reveal whether there is a net metal release or uptake by the sediments under anaerobic conditions. If our results show that metals are removed from the water and immobilized in the sediments then anaerobic bioreactors may be a potentially successful treatment option for mine seepage water in the North. Experimentation will be undertaken within the facilities of the Baldwin lab at UBC under the co-direction of Dr. Sue Baldwin (UBC) and Al Mattes (Nature Works). Two full time undergraduate co-op students will be required for approximately four months to complete this work..

5.1.1.5 Hydrological Factors in Northern Passive Anaerobic Water Treatment (UBC and AEL)

One of the primary variables which determine the success of a passive anaerobic bioreactor is hydrology. If the system throughput is allowed to short circuit (i.e., channeling of flow) then large portions of the reactor become essentially useless as no contact between the biological products and the contaminants can occur. Patrick Barrick, a fourth year student in the Biological and Chemical Engineering Program at the University of British Columbia is currently undertaking a 4th year thesis titled "*Computational Fluid Dynamics: Modeling Subsurface Flow for Passive Treatment Bioreactors"*. The main objective of his thesis project is to use Computational Fluid Dynamics (CFD) to model the hydrodynamics of a subsurface flow (SF) constructed wetland system (i.e., passive biological reactor) and to optimize the mixing that occurs in these systems. This will be achieved by conducting a sensitivity analysis on various design parameters such as aspect ratio, depth, angle of slope and nozzle configurations. The goal of Patrick's thesis work is to achieve a configuration in which minimal short-circuiting will occur. (i.e., maximizing mass transfer and therefore removal of metals). Based on a literature review and CFD modelling, Patrick will construct a bench scale experiment to test the parameters hypothesized to optimize the hydraulic performance of a SF bioreactor Patrick's thesis proposal is appended to this report as appendix A.

5.1.2 DELIVERABLES

At the end of the project, a report will be created for the sponsors describing the work done and results produced. Also, depending on what is found, results will be published in a reputable journal or presented at a conference that disseminates work pertaining to environmental issues of mine environments in Northern climates. UBC, AEL and Nature Works will collaborate with input from stakeholders to prepare the final report. Review will be issued ant 50% and 80% completion. In addition, the WKSS will also be provided with promotional photographs and a plain English summary of the work completed

5.1.3 BUDGET

Table 5 Budget for Future Work

Activity	Unit Rate	Duration	Total
Two Undergraduate UBC Co-op Students	15$/h	4 months	$20,328
Honorarium for Dr. Sue Baldwin Ph.D. P.Eng.	N/A	100 hours	$5,000
2*Nature Works Staff for Site Visit	750$/day	5 days	$7,500
Travel for Nature Works Staff	N/A	N/A	$3,000
Housing and Meals for Nature Works Staff	N/A	N/A	$2,500
Flights to 3 Northern remote mines	N/A	N/A	$3,000

Shipping of Materials to UBC	N/A	N/A	$3,000[8]
Nature Works Staff and Supervision for Column/Mesocosm Study	N/A	N/A	$5,000
Analytical Analysis for Column/Mesocosm Study	N/A	N/A	$6,000
Materials and Supplies for DNA extraction	N/A	N/A	$3,500
Analysis of Sequential Extraction of Sediments	N/A	N/A	$4,000
UBC Undergraduate Thesis Supplies	N/A	N/A	$2,776.35[9]
AEL Labour for site visits and additional research if required	$75/h	75	$5,625
AEL Project Management	100$/h	30	$3,000

TOTAL REQUESTED **$68,453**

5.1.4 BUDGET EXPLANATION

Since it is important for information from this project to be disseminated as soon as possible, the laboratory work will be carried out by two COOP students working together in the UBC Baldwin laboratory. One student will perform the sequential extractions and the other will carry out the microbial identification and mesocosm work. Dr. Susan Baldwin and Al Mattes will actively supervise these students and assist with the experiments in the laboratory.

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[8] Hazardous goods fees may apply, as such a contingency has been factored in.

[9] Undergraduate thesis budget is presented in Appendix A of this report

The second objective will be carried out by a graduate student in the Department of Chemical and Biological Engineering at the University of British Columbia and will commence in May 2006 for a period of two years.

5.2 Phase two (May 2006 – August 2008)

There is strong evidence in the literature that passive treatment processes using anaerobic cells and/or sub-surface flow wetlands are effective, low-cost and sustainable methods for removing metals from mine leachate. Thus, we propose to investigate the application of this technology to mine leachate treatment at hard rock mine sites in the NWT.

5.2.1 SCOPE OF WORK

1.Testing of suitable substrate for anaerobic cells

Anaerobic cells and sub-surface flow wetlands are lined, contained areas filled with a substrate typically consisting of gravel, a carbon source and sand. This substrate supports the growth of bacteria such as SRB. Water to be treated flows through the substrate contacting the bacteria. In some designs, a of mixture limestone, pulp mill biosolids and Fe-oxide sand are used. It is not known what the availability, in the NWT, is of suitable material for this substrate. The first step will be to survey the NWT for the availability of organic substrates that could be used to support bacterial growth. Non-acid generating gravel material is assumed to be widely available on mine sites, but may require some particle size reduction. Once sources for suitable materials have been identified, column tests will be performed in the laboratory at UBC to test the potential of several mixtures to remove arsenic from a typical mine leachate. The latter will be collected from a suitable site in the NWT and shipped to UBC. This will serve also as a proof-of-concept for passive treatment.

2. Computational fluid dynamics modeling for optimization of hydrology

To maximize the treatment performance per unit area, short circuiting of the system should be prevented and dimensions chosen that result in a uniform residence time. A fourth year thesis student at UBC currently is developing a model for subsurface flow wetlands. This model will be used to predict the effect of influent nozzle configurations and wetland dimensions on arsenic removal. Parameters for this model, such as permeability and arsenic removal kinetics will be derived from the data produced in the previously mentioned experimental study. The model uses commercially available CFD software called FLUENT. Results from the model predictions will reveal what length, width, depth and nozzle configuration to use for the subsequent field trials. However, first some verification of the computer model will be done using a small-scale system constructed on UBC campus in a greenhouse.

3. Field trials of anaerobic cell and subsurface flow wetlands at a NWT mine site

Once a suitable substrate mixture has been identified and optimum dimensions chosen for the anaerobic cells, construction of a pilot-scale system is proposed at a suitable mine site in the NWT. The company Nature Works Remediation Corporation will undertake this. Their proposal and budget follows.

INSERT NATURE WORKS PROPOSAL HERE

Budget:

M.A.Sc. student for two years	$16,500 pa
Materials and supplies for laboratory experiments and analysis	$ 3,500 pa

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Appendix A "Patrick Barrick's Thesis Proposal

Introduction:

Over the years mining has occurred all across Canada and because of this it has been a major contributor to Canada's economy. Unfortunately there have been major environmental impacts caused by the early mining years. One of the major issues facing the Canadian mining industry is the treatment of effluent during and after closure of a mining property. [4] One major problem in the mining industry is Acid Mine Drainage (AMD), where acid-generating rock causes heavy metals to leach from waste rock or tailings into surrounding bodies of water. Traditionally chemical effluent treatment has been conducted in Canada to treat AMD, but this has proven to be extremely costly and recently other forms of passive treatment, such as constructed wetlands, have been considered. Constructed wetlands have recently been gaining popularity due to the fact that they are quite cost effective and relatively maintenance free.

A "constructed wetland" is defined as a wetland specifically constructed for the purpose of pollution control and waste management, at a location other than existing natural wetlands.[1] There are two types of constructed wetlands, the free water surface wetland and the subsurface flow wetland and this study will focus on the later type of wetland.

Subsurface flow constructed wetlands first appeared in Western Europe as a wastewater treatment technology in the 1960s. In the 1970s the first systems were being built in the US and by the 1990s there was a large increase in the number of systems being used around the world as the application increased from mainly municipal wastewater to stormwater, industrial and mine water, and agricultural waste waters.

Subsurface flow (SF) wetlands consist of a basin with impermeable sides to prevent seepage and a bed with a suitable depth of porous media. Typically rock or gravel is used as the media type. The wastewater is normally injected horizontally to the bed at a rate that ensures that the water level does not break the surface of the porous media. The systems usually have a slight slope toward the outlet of the wetland to aid in the hydraulic gradient and induce flow. They rely on biological, chemical, and physical processes in a natural environment to treat wastewater. For the treatment of mining waste waters these systems use naturally-occurring bacteria and/or vegetation to either uptake or change the valency of metal-contaminated water and soil. One major issue with SF constructed wetlands is short-circuiting and because of this problem it has brought up concerns with using these types of systems for treating wastewater.

Background/Previous Work:

After extensive research it has been concluded that computational fluid dynamics has not been used to investigate the hydrodynamics of constructed wetlands in the past. Therefore this investigation will be the first of its kind.

To optimize wetland treatment processes, it is beneficial to maximize contact between wastewater contaminants, the wetland substrate and aquatic plants, while minimizing short-circuiting.[2] Short-circuiting is when water is allowed to move through the wetland more rapidly than the theoretical retention time would suggest. The theoretical retention time is based upon a calculation that neglects any influences of obstruction, stagnant regions, and velocity gradients within the wetland. The problem with the theoretical retention time is that it can differ substantially from the actual retention time.

Channelling is a problem because it causes varying flow characteristics in the wetland and this in turn causes different parcels of wastewater to remain in the system for a wide range of times. If each parcel of wastewater does not have an equal retention time than different levels of treatment will occur.

To the present day not much is known about the hydrodynamics of SF wetlands. Many models and equations have been made, but these models have usually assumed that the wetland is either acting as a plug flow or a completely mixed reactor. Although these models are simple and widely used, they do not fully integrate the complex processes which actually occur in wetlands.

The literature shows that a study was conducted that evaluated the influence of the aspect ratio (length to width ratio) and granular medium size on the hydraulic behaviour of SF constructed wetlands by means of a tracer test. In addition, the accuracy of non-ideal flow models (plug flow (PF) with dispersion and complete stirred tanks (CSTs) in series with delay) in describing this hydraulic behaviour was assessed.[3] For this study experiments were carried out in three pairs of SF constructed wetlands that received equal and constant flow of effluent, and that had almost equal surface area with the following aspect ratios: 1:1, 1.5:1 and 2:1. Within each pair of wetlands the granular medium size differed from coarse granitic gravel to small granitic gravel. Each bed was kept at an equal and constant depth. Tracer tests were conducted by a single-shot injection of a dissolution of KBr into the inlet tubes of the beds. From this, concentration versus time curves were created and used to determine which method improved the hydraulic behaviour of the system. From this study it showed that a higher aspect ratio and finer medium improved the hydrology of the system by reducing internal dispersion.

Thesis Objectives:

The main objective of this project is to use Computational Fluid Dynamics (CFD) to model the hydrodynamics of a SF constructed wetland system and to optimize the mixing that occurs in these systems. It is believed that this can be achieved by conducting a sensitivity analysis on various design parameters such as aspect ratio, depth, angle of slope and nozzle configurations. The goal will be to achieve a configuration in which minimal short-circuiting will occur.

The first step to solving this objective will be to create and evaluate a CFD model using Fluent 6.1. First, a steady-state CFD model will be generated, followed by a dynamic simulation to simulate the injection of a tracer. Using information from the aforementioned published study of SF hydrodynamics, two models will be created, with different aspect ratios and granular medium size, which duplicate the systems found in the literature. A tracer simulation will be used to convey the hydrodynamics of these systems. The results from these simulations will be compared with the values from the published article and once similar results are found the models will have been evaluated and will therefore be more reliable.

The next step from there is to conduct a sensitivity analysis on the different design parameters. The design parameters in question are the aspect ratio, depth, angle of slope and nozzle configurations. With time permitting each design parameter will be tested to determine its optimum range. The aspect ratio will be varied over a range of 10:1 to 1:1 while keeping a constant surface area and overall volume. Once an optimal aspect ratio has been determined a study can be done to determine the most efficient depth for that aspect ratio. Media depths typical range from 0.4 to 0.5 m and water depths usually fall within 0.4 to 0.5 m and therefore an analysis with depths close to the these values will be conducted. The next parameter of importance is the angle of slope. To determine the most efficient angle of slope the model with the optimum aspect ratio and depth will be used and the angle of slope will be change from 0 to 1%. Finally various nozzle configurations will be investigated to see which type of layout gives the best performance.

Initially these parameters will all be modelled without implementing any type of model that considers plant roots. If time permits the scope of the project will be extended and a model will be created with roots, which will be represented by cylinders. A typical plant density will be used for this model.

If the CFD modelling is not complete by a certain date or all of the design parameters have been investigated, then an experimental model will be created based on the most recent, optimized CFD model. This experimental apparatus will hopefully be used to once again validate the final model. From this it will be decided whether the final design is reliable or not.

References

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Application for Funding

January 10, 2006

To: Shaun Lamoureux and Alvaro Reyes

Re: Funding Request for Thesis Experimental Equipment

For my undergraduate thesis, Computational Fluid Dynamic Modeling Subsurface Flow for Passive Treatment Bioreactors, an experimental apparatus is needed to validate the results from the computational study. This will involve building a small scale constructed wetland based on the final computational design. The goal of this project is to gain a better understanding and to improve the hydrodynamics of constructed wetlands. To build this apparatus a material cost of $2776.35 was determined. A detailed list of the materials can be seen below.

Supplies Needed	Amount		Price
Potassium Bromide (Tracer)	(500 g)		$150.00
2x4	150	ft	$100.00
Braces	112		$350.00
Sheets 3/4" plywood	12	8'x4'	$300.00
Gravel	61.25	ft^3	$300.00
Pump			$280.00
Hosing/Piping			$100.00
Storage Tanks			$200.00
Pond liner	160	ft^2	$100.00
Screws	2	boxes	$50.00
Tools			$300.00
Total			$2,230.00
Tax			$323.35
Contingency (10%)			$223.00
Total			**$2,776.35**

If there are any concerns or questions about this request I can be contacted at (604) 266-7553 or at patrickbarrick@gmail.com. I want to thank you for spending the time to look at this request.

Regards,

P. Bar

Patrick Barrick
Undergraduate Student