An Evaluation of Environmental Effects and Remediation of Toxic Elements in Metal Mines

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2022-07-20

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Acknowledgment

This project was supported by Professor Les Lavkulich, without his exceptional support it would not have been possible. His encouragement and advice have kept my work on the right track. And a special thank you to our academic coordinator, Julie Wilson. I also want to thank my colleagues from MLWS who provided insightful comments and expertise that greatly assisted the project. I am grateful to all of those with whom I have had the pleasure to work during this and other related projects in the last year.

I would like to thank my family and friends, whose love and support I cannot neglect, and all the mentors I had during my six-year education at UBC.

Executive Summary

Heavy metal pollution by mining activities can occur in a wide range of regions across BC. Improperly closed mines can create serious long-term environmental and health impacts. For example, the Pinchi mercury mine, and the Britannia copper mine remained to be some of the most polluted areas even decades after closure. The Bralorn-Pioneer gold mines were left a ghost town without any remediation until they came back to production in 2017.

The level of metal contamination can be affected by many factors, including the main ore type, the structure of the mines, geological setting, climate, etc. With different combinations of natural settings and different mine structures, each mine can create environmental problems in its unique way. Therefore, remediation planning cannot be limited to a series of actions targeting individual problems after mine closure, but to be provided along the designing and operating stages.

This project aims to examine the differences between different mines in BC by reviewing past geological surveys, remediation reports, and related pieces of literature. The project found that microbes with performance-enhancing amendments can treat problems such as AMD in metal mines. However, more field-level work needs to be conducted to accurately assess the ultility of microbes.

Introduction

The mining industry is an important pillar of the global economy. However, without proper management and accurate accounting of its total environmental impacts, mining can severely pollute the atmosphere, water, and soil. Evidence has shown that almost all the environmental effects caused by mining as well as other activities can be seen as cumulative effects because systems are modified by humans and most of the systems are connected. Individual effects combined over time and area are the deciding factor in final environmental consequences, rather than direct single action. Metal mining is a large operation that starts to pose effects on the environment from the operation stage until long after it's abandoned (Oburanti, et al 2020).

Metal mining creates contaminants including dust, toxic gases, and greenhouse gases, such as s, including SO2, NH3, H2S, NO2, NO, and CO, from the exhaust during the creation and operation (Yan et.al., 2019). Soil and water around mine sites include ash, flue dust, gangue, industrial minerals, loose sediment, metals, metallurgical slag and wastes, and the creation of large, contaminated tailing ponds (Ayangbenro et.al., 2018). Mine tailings are often mixed with water and discharged as a slurry into large tailings dams (Price & Errington, 1998). Tailings materials often contain sulfide minerals, like pyrrhotite (Fe1-xS), pyrite (FeS2), arsenopyrite (FeAsS), and heavy metals, like mercury, arsenic, and lead. These sulfide materials will oxidize upon exposure to water and oxygen or ferric iron and generate acidic, metal-rich leachate known as Acid Mine Drainage (AMD) (Méndez-Ortiz et.al., 2007; Price & Errington, 1998). AMD creates a hostile environment unsuitable for most organisms with a high concentration of mobile heavy metal and low pH. If the tailing pond leaks, contaminated water can enter the adjacent ecosystems or even water supply systems, producing public health issues and making it especially difficult to remediate. In many cases, the wastewater stream from tailings enters some nearby water bodies without treatment, resulting in a larger area of degradation (Méndez-Ortiz et.al., 2007).

Understanding the overall effects of metal toxicity from mining is critical for making remediation decisions. Although the Canadian Environmental Assessment Act (Updated in 2012) added the cumulative effects assessment as part of the policy to capture long-term effects on the environment and society, it is not mandatory to calculate cumulative effects in most provinces, and the standards of cumulative effects vary. Moreover, each mine has different features including geology, environmental settings, and different problems with regard to heavy metal production. Most environmental assessment work focuses on analyzing a single activity rather than focusing on multiple activities or stressors that may occur in the same region The lack of studies connecting embedded geological and climatic conditions with mining remediation makes it hard to compare and produce any universal protocol for a guaranteed result.

Although it is difficult to capture the whole picture of cumulative effects, looking at the connection between systems instead of single events can result in more effective remediation. This project attempts to integrate some of the principles of cumulative effects assessment to study some major mine sites in BC from a holistic point of view. Starting with the understanding that metal bioavailability is not necessarily a simple function of total metals. It is affected by various physicochemical and biological factors largely dependent on the natural setting of the site (Smolders et al., 2009). By reviewing how some of the major heavy metal pollutants are being released, transported, absorbed, and transformed through the hydrological and biological cycles, this project can affect remediation decision-making. Instead of focusing on the total concentration of metal in soil and the adjacent water or protecting a few key species, mining remediation should prioritize maintaining the connections and functionality of the natural systems so that the region can be fitted in with the surrounding ecosystem sustainably. To achieve such a goal, remediation actions need to be taken at the starting stage of the mining operation and act as a guide for operation, instead of a post-operation remedy.

Three mines in BC were chosen as case studies: Bralorne-Pioneer mines, Britannia mine, and Pinchi mine. Each mine has different ore and surrounding areas. Bralorne -Pioneer mines were an old gold mine located in the Gold Bridge area and heavily polluted with arsenic. Britannia was once the largest copper mine in British Commonwealth countries. Its adjacency with multiple creeks and Howe Sound expands copper, zinc, and cadmium. Pinchi mine extract and roast cinnabar to recover mercury, which releases toxic mercury into the soil, water, and air. My project will explore their unique properties and how those properties affect metal toxicity.

Objectives

The main objectives of this report are the following:

a). Provide a holistic view of how toxic elements from mining activities affect the surrounding environment by identifying the major environmental sources of contamination.

b). Analyze mine sites in different areas in BC to explore the link between geological conditions and metal toxicity.

c). Provide a new and holistic perspective to remediation planning.

Methods

The methods used for this research are based on a systematic literature review and the analysis of significant case studies. Relevant works of literature were chosen from published journal articles and reports, theses, and governmental records. Starting from the arch-level impacts of metal mining and Acid Rock Drainage, the project focused on three mines in British Columbia containing several main heavy metals: arsenic, zinc, cadmium, copper, and mercury. Old geological surveys for the cases were analyzed to find the link between metal behavior and their geological characteristics. By analyzing the results of the three remediation operations, a final recommendation was made to ensure reclaimed mine sites can adjust to the surrounding environment.

Mining contamination of soil and water

Oxidation of Sulphides

The toxicity of AMD polluted tailing is caused primarily by low pH and high heavy metal concentration (Newsome and Falagán, 2021). The synergistic effect between acidic pH and metal solubility increases the bioavailability of heavy metals, thus, increasing biotoxicity. Exposure to these unfavorable conditions introduces stress responses. Microbial cell morphology and assembly change and these changes restrain cell growth. Certain enzymes can be broken by the acid and limit metabolic functions. Both physical and biogeochemical processes control the production of AMD. Water content, oxygen diffusion rate, and infiltration rate in the tailing can be influenced by soil texture. Different types of heavy metals also affect the toxicity and spread of contaminants.

The overall reaction for pyrite oxidation in water with access to dissolved oxygen (DO) is written according to Equation 1, where ferric hydroxide, sulfate, and 4 protons are produced

(1) $FeS_2 + 3.75\ O_2 + 3.5\ H_2O \rightarrow Fe(OH)_3 + 2\ H_2SO_4$

Pyrite oxidation in water with access to DO may also be written according to Equation 2, where ferrous iron, sulfate, and 2 protons are produced

(2) $FeS_2 + 3.5\ O_2 + H2O \rightarrow Fe^{2+} + 2\ SO_4{}^{2-} + 2\ H^+$

Bacteria like *Acidithiobacillus ferrooxidans* obtain energy from the oxidation of ferrous iron and elemental or reduced sulfur compounds (e.g. metal sulfides), using DO as the electron acceptor under oxidizing conditions (Equation 1), and thus catalyze the oxidation of iron and sulfide minerals. Figure 1 shows the formation of AMD with the roles of microbiomes during the process.

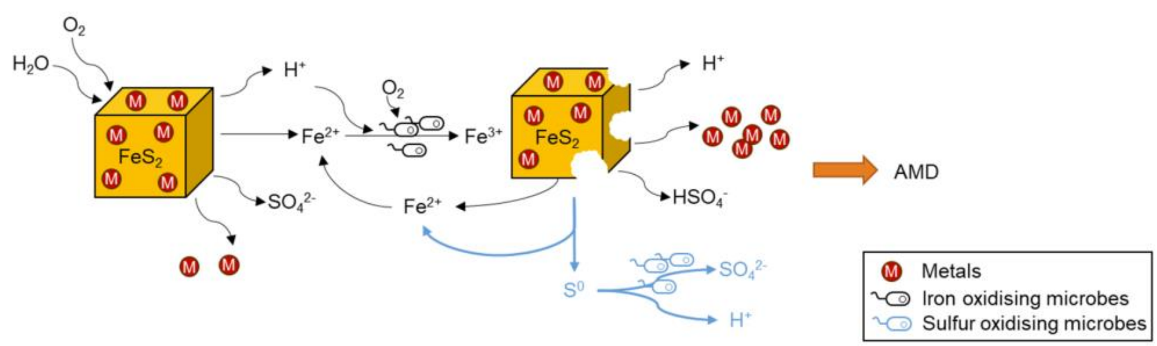

Figure 1 The process of AMD formation (Newsome and Falagán, 2021)

Different types of watersheds can alter the physical, chemical, and biological processes in the tailings (Figure 2).

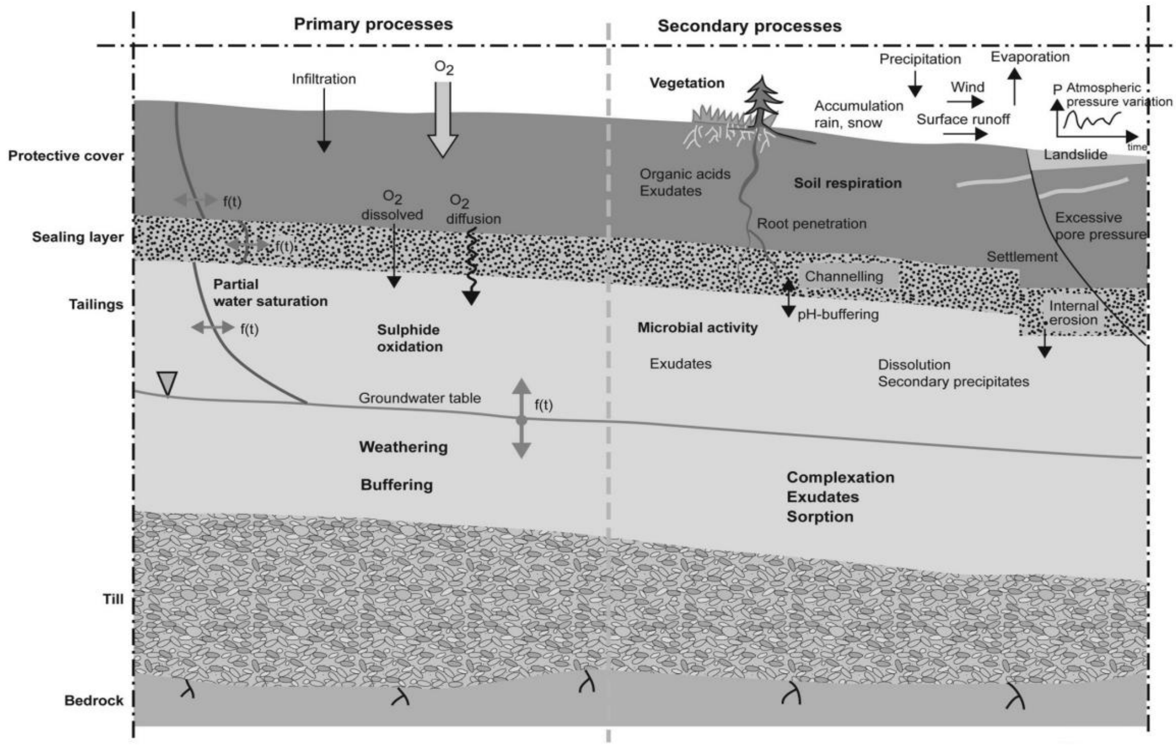

Figure 2. *Major physical, chemical and biological processes in soil covered tailings (Gleisner, 2005)*

This paper will focus on several main heavy metals in the metal mines in BC that are considered challenging and dangerous to remediate: arsenic, mercury, zinc, lead, and cadmium during the mining process for copper, mercury, and gold.

Case 1—The Bralorne-Pioneer Mine with high-arsenic drainage

Background (Geology, climate, and main ore)

Bralorne-Pioneer mines are located in Bridge River Valley, carved into the Cariboo Mountains just five hours northeast of Vancouver. The mine is located in the Coast Mountains rain shadow and lies between the West Coast Marine and Interior climate zones. The highest average air temperatures occur during the summer (July and August) with the highest temperature ranging from 20°C to 25°C. Winter and snow season is long with January being the wettest month (rainfall 226mm). The month with the highest snowfall is December (848mm), and the snow-free months are June, July, and August (Weather Atlas, 2022). The region's geology is dominated by two main lithologic assemblages that comprise basalts, thick accumulations of ribbon chert, ultramafic rocks, and minor limestone and coarse clastic rocks. Defined by fault-bounded boundaries, the Bralorne property comprises major Northwest and North-trending faults, including the Fergusson fault and the steep Cadwallader fault. The whole regional geology with the fault system is shown in Figure 3. These two major faults form the gold-quartz-containing veins where the Bralorne mines and Pioneer mines are located. A signature feature of the Bralorne-Pioneer deposit is the intense wall-rock alteration with vein layer formations and gold-deposited greenstones. It is also characterized by its high carbonate content and low sulfide content (Leitch et.al., 1991). Vein formation is accompanied by heated aqueous fluids along with fractures and grain boundaries, creating hydrothermal alteration envelopes, characterized by the addition of K_2O, CO_2, S, As, and Au and depletion of Na_2O and FeO total. Because of the low sulfide content, AMD is not a usual concern for this type of deposit. However, water that originates from contact with the ore and altered wall rocks has a neutral to alkaline pH which increases the mobility of As and Sb, thus the environmental problems are still serious even without AMD (Desbarats et.al., 2014).

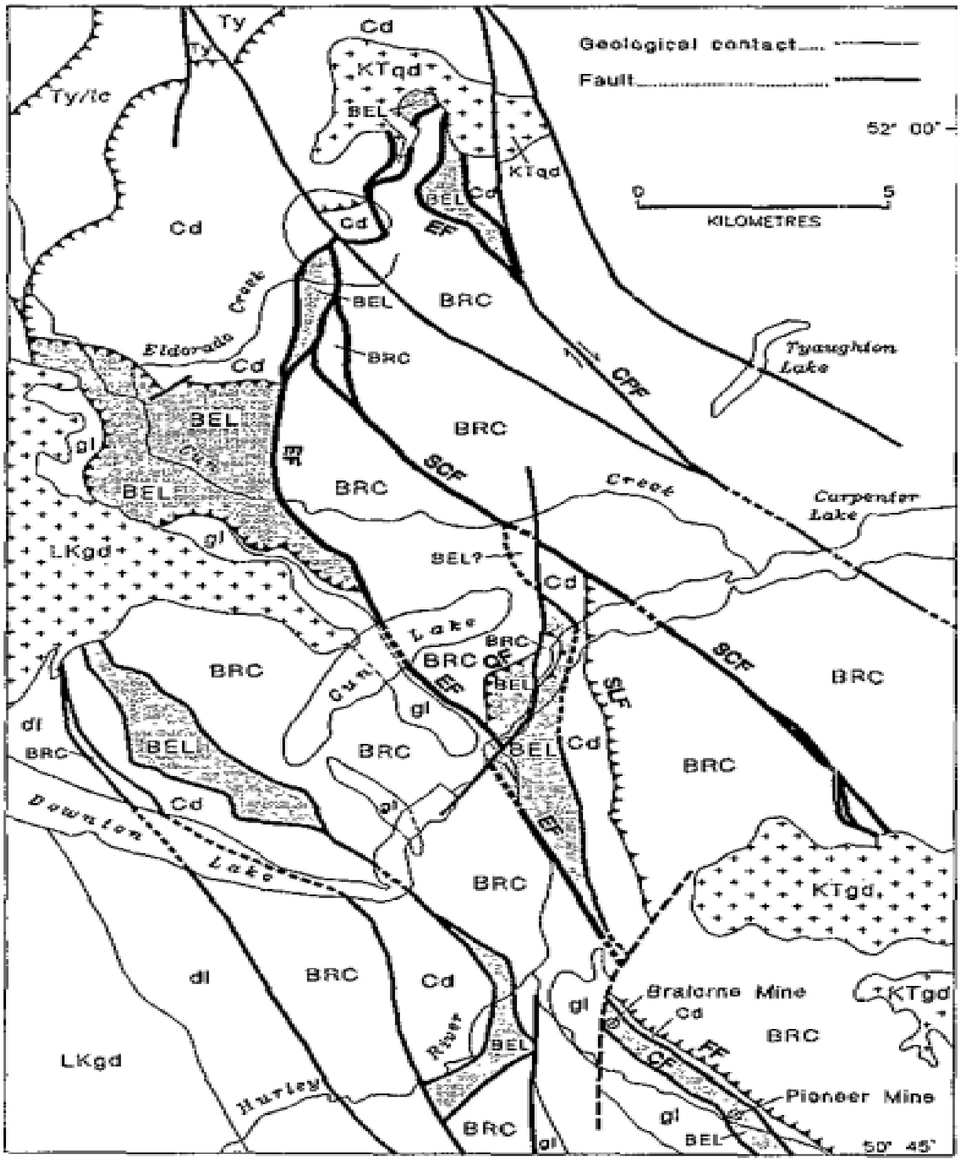

Figure 3. Simplified map of the Eldorado fault system. CF=Cad-Wallander fault; CPF=Castle Pass fault; EF=Eldorado fault; FF=Fergusson Fault; QF=Quarry fault; SCF=Steep Creek fault; SLF=Sucker Lake thrust fault. KTgd=granodiorite of the Bendor plutonic suite; KTqd= Eldorado pluton; LKgd=Dickson-McClure batholith.(Schiarizza and Garver, 1995.)

The effects of geology on As species are evident in the Bralorne-Pioneer gold mine in Bridge River Mining District (Schiarizzs et.al., 1997). The sulfides are dominated by pyrite, arsenopyrite; stibnite, pyrrhotite, sphalerite, and chalcopyrite. On the surface, the top strata are characterized by alpine rock complexes which include rock, colluviums, and till. Alpine and glacial landforms create thin topsoil and the main vegetation is spruce and Douglas fir. These geological factors and the associated diverse mineral differentially impact the occurrence, speciation, distribution, transport, and uptake of As. Cadwallader Creek runs Northwest bringing the metalloids from vein upwelling, carrying the metalloids with it. Desbarats et.al. (2015) tested the flume of the discharge at the main haulage adit (800-level portal) for the total concentrations, filtered concentrations, and the particulate concentrations of metals. They found that during 3 years, the total concentrations of As and Fe were closely related to higher discharge rates and the proportion of fine sediments. Most of the As was transported in the dissolved phase and most of the Fe was transported by the suspended particulate phase. This result of the process releasing As (III) and dissolved Fe dropped sharply within the 500 m range of the discharge point (Figure 4 a.). The process indicates that Fe oxyhydroxides are precipitating rapidly, and As is being co-precipitated along with gradual oxidation of dissolved As (III) to As (V).

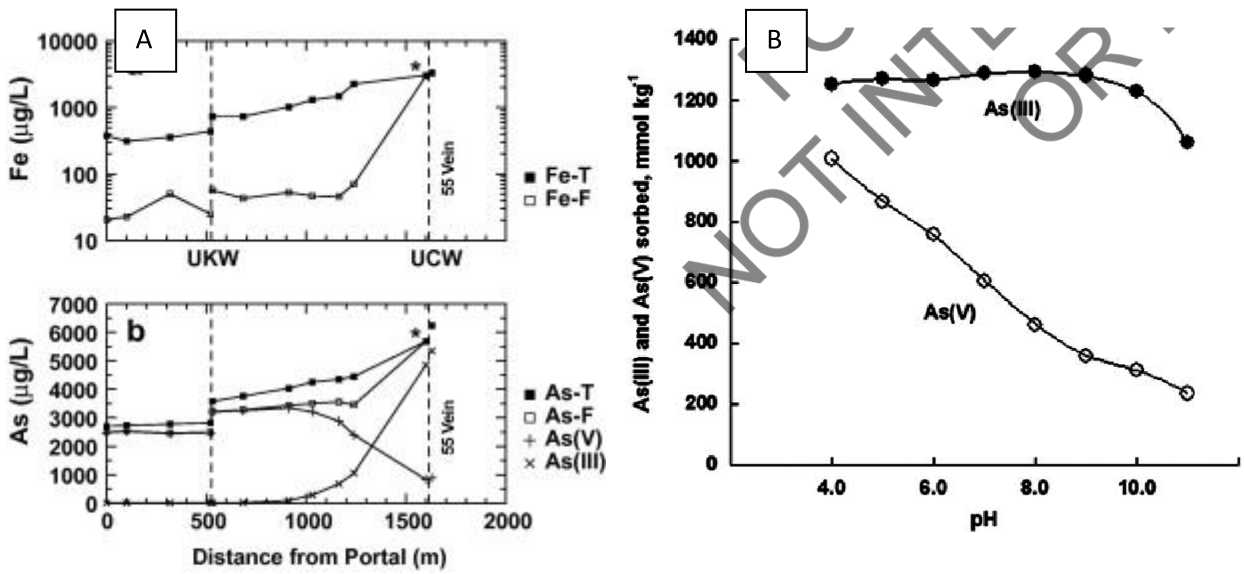

Figure 4 (A & B). (A.) The concentration of Fe and As in relation with distance from the portal (Desbabra et,al., 2014)) and (B.) As species distribution with changing pH level (Pigna et.al., 2015).

In a given pH range, the sorption of As (III) and As (V) changes. (Figure 4 b.) In general, As (III) has a greater sorption capacity. However, how much As can be adsorbed to soil particles depends on the existence of many other metalloids. The “competition” between As and other minerals is the key to defining its mobility (Farooq et al., 2016a; Srivastava et al., 2020). The mobility of As and other metalloids can affect their interactions with plants and in turn, enter the ecosystem (Figure 5). Particularly, the phosphates (P) and As possess similarities in their chemical structure and use the same transport system (Khan et.al., 2021). Firstly, As from the soil is transported to root cells via phosphate transporters, silicon transporters, and aquaporins. Some As are made complexes with plant phytochelatin complexes, and the remaining is being effluxed by phosphate and silicon transporters and loaded into xylem vessels, thus translocating As from roots to shoots. The transportation from shoot cells to grain cells is assisted by phloem. In addition to the effects of the plant cell, the uptake, translocation, and accumulation of As in different plants largely depends on soil properties, nutrient level, and microbial communities. Under nutrient-stressed conditions, plants are more likely to gain nutrients from As-bearing minerals, thus causing more As to be released into the soil (Beauchemin et.al., 2012].

Contamination of soil and water

Arsenic is one of the major sources of metal-mining pollution, it usually appears in the form of As (III) or As (V), with mercury. Elevated arsenic and sulfate concentrations in Long Lake, a lake in the Quinsam watershed, British Columbia, suggested the freshwater system is affected by mining operations in the watershed (Schiarizzs et.al., 1997). Arsenic concentrations at different depths of the lake and sediment were tested. The results showed a high concentration of arsenic in surficial sediment caused by the direct input of iron oxide hydroxides bonded with arsenic into the lake from point sources a mine-impacted lake seep, and indirect sources through the sorption of dissolved arsenic precipitated iron hydroxyl species. The evenly elevated level of arsenic in deep sediment and near the seep without any cluster of arsenic around the seep indicates that the lake sediment is not just from settled seepage. Further dating of the sediment core found that the arsenic accumulation in the sediment started around the time when the mining operation began, and coincident with the sulfate level (Moriarty et.al., 2013).

Studies of arsenic have shown that the detrimental effects on humans and the environment primarily occur when As is in a highly mobile form, and is released into shallow groundwater and diluted and discharged into a larger watershed. Rather than total concentration, the biological availability or potential toxicity of metalloids depends on their chemical speciation. During the process of metal speciation, chemical, physical and biological reactions in the soil differentially affect the solid and solution phases of As and regulate its interaction with the plant-soil system sites (Khalid et al., 2017). Therefore, to understand the full impact of As or any heavy metal, it is important to evaluate the chemical speciation of these metals in addition to only measuring the total concentration. Soil and water contain both organic (arsenosugars, arsenobetaine, and monomethyl arsenic acid), and inorganic As in four oxidation states as As (0), (III), (-III), and (V). (Panda et al., 2010). Limestone and dolomites have been reported with an average As concentration of 2.6 mg kg^{-1} (Govindaraju, 1994). The most common As forms in the soil are the sulfides, such as realgar (As_4S_4) or orpiment (As_2S_3), or oxides such as arsenolite (As_2O_3). In cores of some mine sites, arsenic often is present in the form of arsenopyrite (FeAsS). As (III) and As (V) are the most mobile and toxic states of As that exists at mine sites (Khalid et al., 2017). Depending on the pH and redox condition of the soil, the most predominant forms of As are H_2AsO_4, $HAsO_2$ 4, and H_3AsO_3.13 In reduced soil conditions, such as tailing ponds or wetlands, the predominant form of As is arsenite which is 60 times more mobile, soluble, and toxic than As(V) (Warren and Alloway 2003).

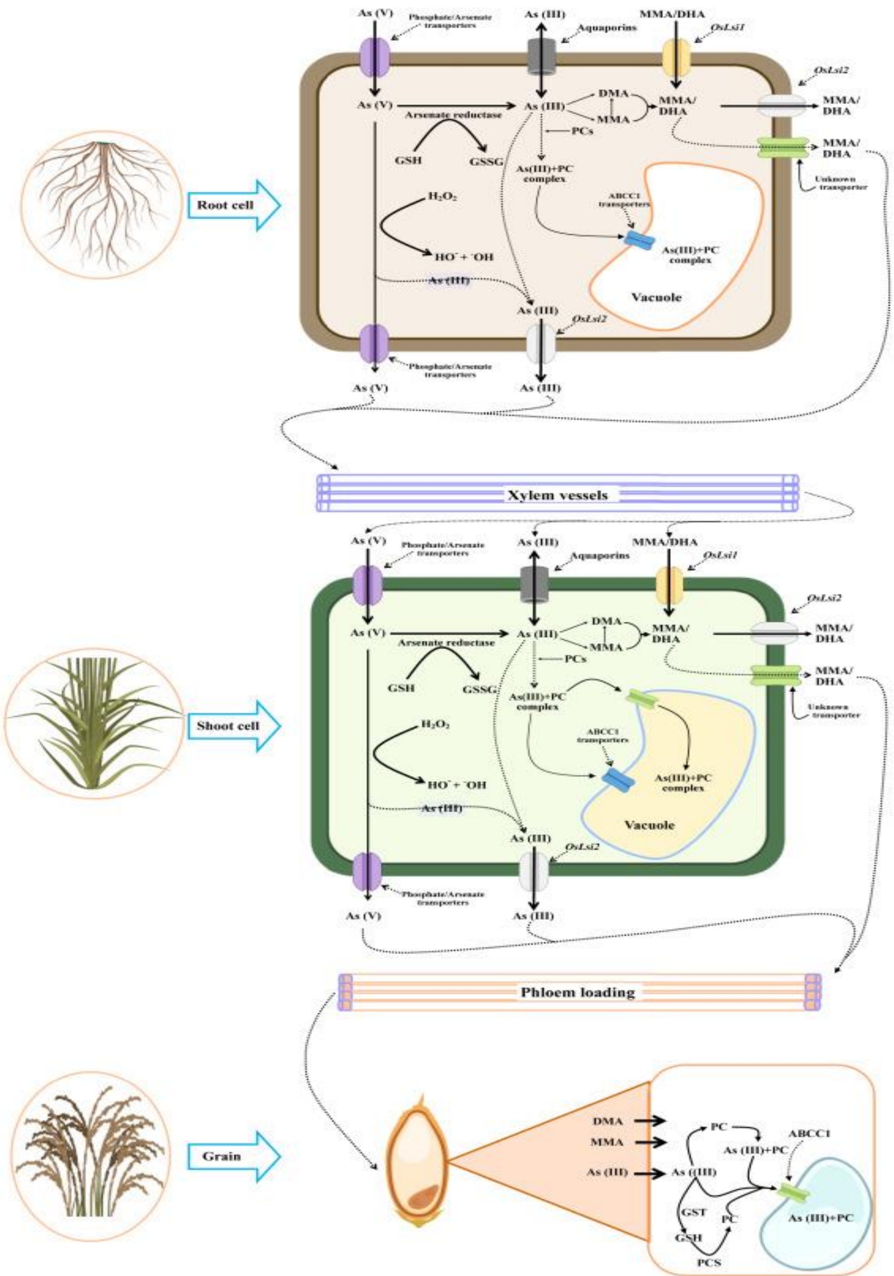

Figure 5. The schematic diagram shows how plants uptake and translocate arsenic, and their efflux ad detoxification pathways (Khan et.al., 2021).

Remediation

The main respond agency for Bralorne Mines is Talisker Resources Ltd. The company has had full control and ownership of the mine since December 2019, after acquiring the ownership from Bralorne Gold Mines Ltd (BGM). Since then, the company has completed a series of rehabilitation actions including timber set rehabilitation geological surveys, mine dewatering, 3-

km truck drift rehabilitation, mine planning, monitoring, and inspection (Talisker Resources, 2021).

The Bridge-Seton Metals (BGM) and Contaminant Monitoring Program in 2015 found that on November 3, 2017, BGM received approval of the Interim Closure and Reclamation Plan (ICRP) through an Amended Mines Ac Permit, M-207. The goal of the plan included the following: long-term preservation of water quality and aquatic environment; long-term preservation of engineered structures; natural integration of reclaimed area to be compatible with the surrounding landscape; proper removal and disposal of waste materials; and establishment of a self-sustaining cover of vegetation (Talisker Resources, Bralorne Gold Project, 2020).

The remediation plan took a long time to make along with many geological surveys and will require a significant amount of money and resources. If the planning was to be started during the earlier stage of operation, the extended contamination would be more controllable.

Case 2. Britannia Copper Mine

Background on Geology, climate, and main ore

Britannia Mine in British Columbia is another source of heavy metal pollutants including Cd, Cu, Pb, and Zn. (URS, 2002) In the 1920s, the Britannia mine was the largest copper mine in the British Commonwealth. During the time the mine was operating, it expanded from a hill at an elevation of 1400 m to below sea level, with five open pits, large tailing ponds, and a series of tunnels, making it difficult to keep contamination under control. As Britannia's openings are in the side of the mountain instead of downward shafts, the adits were connected by a series of raises driven upwards from lower levels. Such connected adits reached Jane Basin floor and became ore draw points which trapped snowmelt and rainfall, encouraging oxidation of sulphide minerals in the waste rock and carrying metal salts down into the mine (McCandless, 2016). Although there were plugging operations done to reduce AMD-caused heavy metal from leaking into creeks, dispersion from open pits still led to high concentrations of trace elements. Heavy rainfall in winter resulted in a large amount of metal-contaminated water flowing from the mine site. Snowmelt from June to August also gives a second peak to Britannia Creek (Golder Associates Ltd, 2003).

The general geology of the Britannia Mine is determined by a series of Jurassic volcanic, sedimentary and plutonic rocks. The geological processes occurred along the Coast Range batholith which contains most of the copper deposits of the Pacific Mineral Belt.

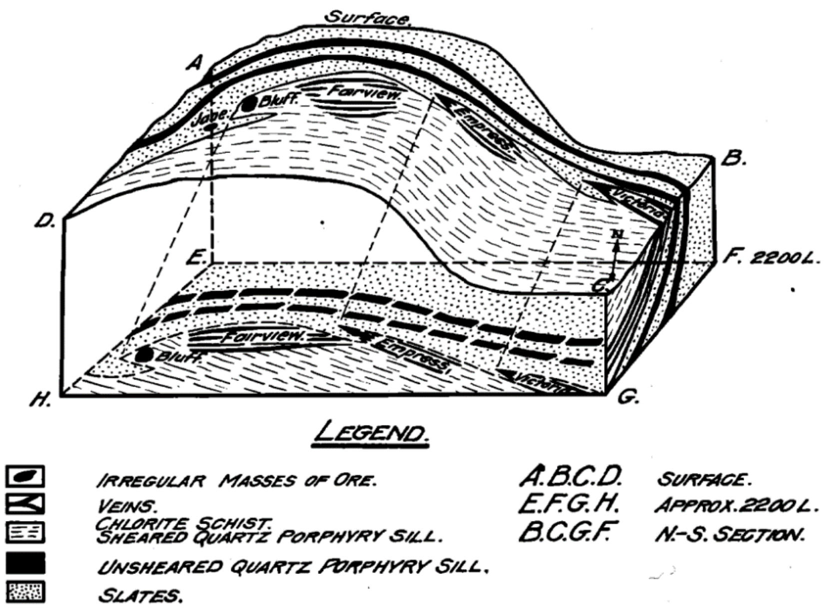

Figure 6. The Block diagram shows the geology of Britannia Mine (Schofield, 1926)

Volcanic activities formed black slates and the angular pieces of volcanic rocks embedded on the slates, and formed a matrix of tuff (Figure 6). The neighboring area of the Britannia Mine consists of slates with a light green-greyish called chlorite schist (Schofield, 1926).

The Britannia ore body is a massive sulfide deposit built upon the chlorite schist. The quartz diorite in the immediate vicinity of the mineral shear zone contains chalcopyrite and pyrite (Chretien, 1991). This makes the area vulnerable to AMD.

The whole Howe Sound Basin can be divided topographically into two parts: the island-strewn basin ranging from a 2 km-wide channel to a 20 km-wide mouth; and the steep, narrow upper basin. Because of the location of the mine, wastes that entered Howe Sound were extensive, random, and highly impacted by the flows from the fjord, especially the fresh, turbid water from the Squamish River (Grout et.al, 2001). Before any remediation efforts, approximately 5 million m^3 of water with an average pH of 3.5 was discharged to Howe Sound annually (O'Hara 2007). Furthermore, the dispersion of metals from these spoil heaps was increased due to heavy rainfall causing general erosion and dissolution. The railway and roads in the region were built using the spoil, consequently further dispersion of contaminants in the region.

Bioaccumulation of trace elements in spruce needles and barks, as well as animal-raised concerns about the effects of heavy metal toxicity (Wilson et.al., 2004). High precipitation in the region makes the remediation work more difficult. The nearby town of Squamish receives an average of 2400 millimeters of precipitation per year. Large amount of precipitation falls into the mine workings and then falls from the two adits, and then flow into adjacent creeks (Environment Canada, 1981-2010).

The concentration of Cu, Cd, and Zn in estuarian surface water ranged from 0.8-230, 0.02-2.9, and 1.7-450 ug/L, taken from a location approximately 350 m from the mouth of Britannia Creek (Chretien, 1995). The variable metal concentrations are largely due to varied seasonal creek discharge. When metal concentrations cross one order of magnitude, metal loading is amplified over 2-3 orders of magnitude. The correlation between discharge and concentration maxima implies that metal concentration increases to a greater extent when the discharge increases (Figure 7). This can be explained by the metal accumulation during dry seasons. During summer, the oxidative dissolution of the ore accumulates as underground work continues. When the rain begins, the accumulated AMD is flushed into the creek, leading to the first stage of increasing metal loading. The second peak is caused by the spring snow melt, after a period of low rainfall during winter (Chretien 1995; Robson 1990). The water from the highest portal, however, showed no seasonal change in Cu and Zn concentrations because the majority of rainfall did not fall into the mine (Goyette and Ferguson, 1985).

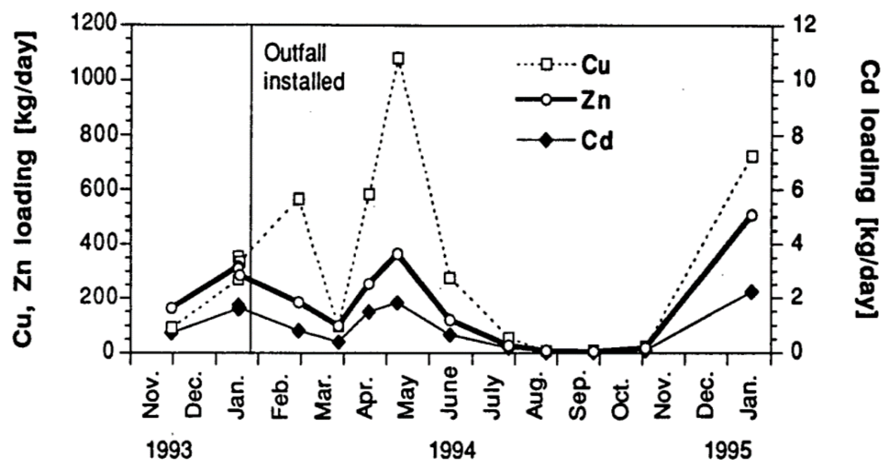

Figure 7. Loadings of total Cu, ZN, and Cd in Britannia Creek (Chretien 1995) .

Contamination of air, water, and soil

Cu, Cd, and Zn are required micronutrients for most organisms, but higher levels lead to toxicity. They are similar in their stability of ionic form, but Cu differs from the other two because of its greater chemical reactivity. Cu+ is readily oxidized to Cu2+, which is the foundation of its biological electron transfer reactions. As Cu is the hardest acid among the three, it is the most likely to complex with O and N and form metal-organic complexes (Chretien, 1991). A study on reeds found that all three metals are concentrated in the belowground part. Cu increased in all parts (belowground, stem, and leave), but especially in leaves in the late season. Zn showed a strong increase in roots and stems, and Cd increased mostly only in belowground parts. Metal toxicity led to the deformation of aerenchyma cells and the disruption of epidermal cells. Air cavities in roots decreased because roots directly contact metal-polluted water. Root hair expands the surface area of the root system, and root exudates can alter root chemistry to increase plants' tolerance toward metal toxicity in those spaces. The number of root hair also decreased due to toxicity and led to a lower amount of root exudates which further weakened the plants' ability to keep toxic elements out of the plant-sediment border (Nawrot et.al., 2021).

Given the nature of Britannia's geology and climate, the AMD condition here is largely controlled by peak flows, thus controlled by the proportion of mixed discharge from the creek and the highest mine portal 4100. Al and Fe content also show seasonal patterns because the high turbidity from early spring brings more suspended terrigenous matter. Since all metal concentrations are uniform throughout the year, the geochemical behavior of Cu and Zn and their interaction with organisms living in the region are seasonally varied.

Many species in the estuary are under the influence of the excess amounts of Cu and Zn, including Blue Mussel and common rockweed. (Fritioff et al., 2006; Grout et al., 2001) Mussel growth was affected by the elevated level of Cu and Zn found in their tissue (Cu concentration was above 20 µg/g dry wt.). Impact of AMD on phytoplankton showed similar trend with a strong seasonal impact (results in July and November being more equivocal indicating the turbidity of Squamish River has an impact on metal concentration) (Levings et al., 2005). The first remediation action was conducted in 2001, two years after the Levings et al. (2005) study was concluded. Records before remediation showed detrimental effects on primary productivity of the ecosystem when several hundred kilograms of dissolved copper and zinc are currently discharged from Britannia Mine into Howe Sound every day (Barry et al., 2000).

Remediation

The remediation plan for two freshwater watersheds in the Britannia area: Britannia Creek and Furry Creek. Based on the Waste Management Requirement Act Order and the Mines Act and Health, Safety and Reclamation Codes for Mines in B.C (2021) the remediation plan had four objectives:

1). Reduce the discharge of harmful substances to ensure naturally habitable areas can recover to an acceptable state; 2). Protect and promote recovery of aquatic and territorial habitats and communities; 3). Achieve and maintain acceptable levels of risk to health and humans and other territorial organisms; and 4). Implement remediation in a cost-effective and timely manner.

To achieve these objectives, both immediate and long-term actions were taken. Construction of plugs and immediate removal of pond sediment and soil adjacent to the mill building controlled any further pollution from the mine's hazardous materials. Stormwater interception and groundwater interception were constructed in the Britannia Creek alluvial fan area and waters were re-routed into a deep outfall. Surface water was also re-routed. In addition to these immediate measures, the re-designing and construction of the mine water collection facility, longer-term water quality monitoring, and water treatment plants were planned for completion within two years since 2003 (Golder Associates Ltd., 2003).

Based on the information gathered, ending Britannia's pollution posed an intractable technical problem for three reasons: the rocks, the structure, and the climatic setting. However, the current remediation plan is too late for solving some of the problems. For example, the mine cannot be sealed by plugging the adits because this would cause groundwater inflows to rise within the mine. Such failure is determined by the design of the mine (McCandless, 2016). The diversion of the surface water route from entering the mines is difficult to implement due to the complexity of the area. All the diversions combined can only reduce approx.10% of the total inflow to the mines. Other concerns regarding costs and regulations make AMD remediation will take longer than planned (Golder Associates Ltd., 2003). Making operation planning with the end goal of remediation in mine from now on would solve the problem from its root.

Case 3. Pinchi Mines with a focus on Mercury and Lead

Background (geology, climate, and main ore)

Pinchi Mine was BC's largest mercury mine, located in the Central Interior of BC, east of Pinchi Lake. The mine operated in two phases between 1940 and 1975 and went into maintenance until 2010 (Bruce et.al., 2013). During the operation period, cinnabar ore was processed from both aboveground glory holes and underground mining to recover mercury. After 1944, the mining methods were updated using fine grinding and floatation to separate the tailings. The operations in the 1940s occurred before mercury's effects on the environment and human health were well known, and both the waste rock and the residue from roasting cinnabar entered Pinchi Lake without any treatment. In more recent operations, wastes are routed as a slurry into a large on-site attenuation pond, but there were still unmanaged sites Studies on fish, decades later, showed excessively high levels of mercury concentrations (Azimuth, 2012).

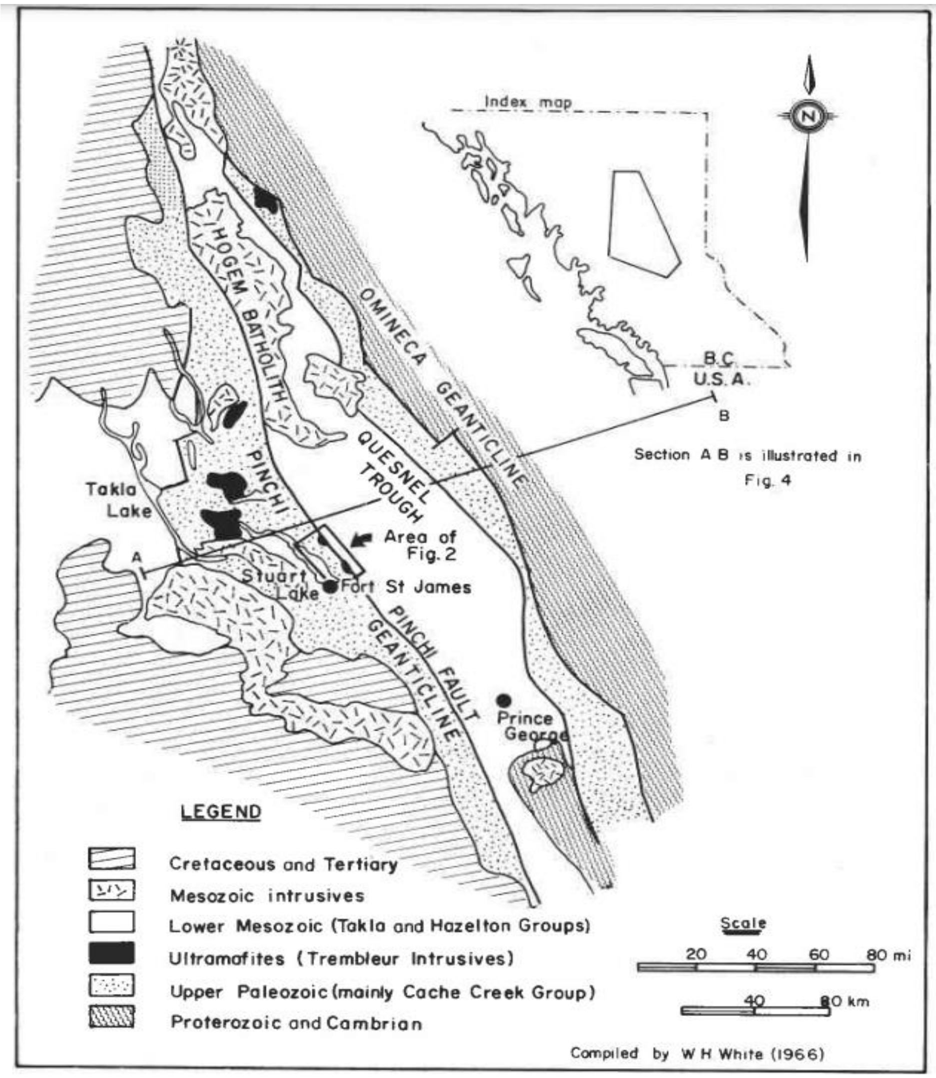

Figure 8. Regional geology and ultramafic minerals map (Paterson, 1977).

As Hg's bioavailability is largely controlled by pH, the regional geological characteristics of the Lake become important for understanding the region's geology is defined by the Pinchi Fault, which extends for 450km in Central BC. The region can be divided into two regions: the lower Mesozoic Takla Group in the Northeast and the Pennsylvanian-Permian Cache-Creek Group in the Southwest (Figure 8) (Paterson, 1977). Mesozoic Takla Group composed of greywackes, conglomerates and minor limestones. Southwest of the fault system is the Pennsylvanian-Permian Cache Creek Group, made up of limestones, cherts, argillites and greenstones (Ghent, Tinkham & Marr, 2009). As mercury naturally occurs from the mercury belt in the faults, it tends to form highly stable organic compounds, and can become naturally concentrated in humus through long-term uptake by plant. The decaying plant material would then return mercury back to the humus layer (McMartin, Henderson, Plouffe & Knight, 2002). With the illuvial deposits near the lake, organic forms of mercury are largely being trapped, especially within 10km of the mine. The lake created high quality surface organic horizons which enabled high solubility of the metal constituents, plus a high degree of anthropogenic metal loading, created a high-concentration mercury zone in top soil. In heavily polluted zones (<5 km to the mine), mercury can leach to C zone (Äyräs & Kashulina, 2000).

Contamination of air, soil, and water

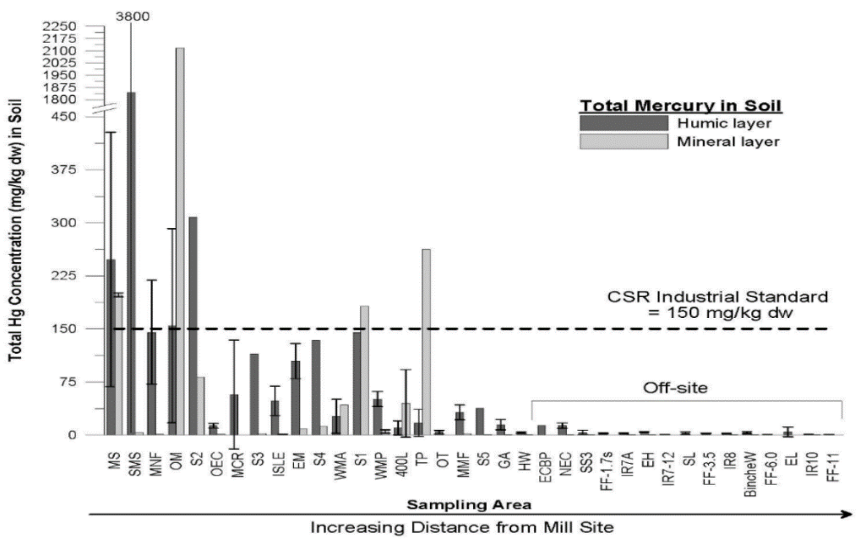

Figure 9. Total mercury concentrations in humic and inorganic soil layers in Pinchi Mine with a spatial gradient, from 2004-2007. (Allard et.al., 2013).

Mercury is unique for its various naturally-existing forms at ambient temperatures, making it a polluting source for both soil and air. Mercury, as a vapor may be carried along with the prevailing wind directions, and the contaminated areas expand due as non-point source mercury accumulation (Allard et.al., 2013). Atmospheric mercury can also be sequestrated by plants, especially trees, and may be further released into the soil. Hg in the atmosphere exists mostly as Hg(0) vapor but can be complexed by humic acids and iron oxyhydroxides (matrix-bound Hg) (Navarro et al., 2006). Although most Hg species have low solubility, Hg(II) and the organic MeHg can translocate from soil to shoots. Plant leaves can also directly take up Hg vapor and reemit it via absorption, and a large amount of Hg can enter the roots from the soil via transpiration streams. Both dry and wet deposition of MeHg species is also possible making plants an effective pathway for mercury translocation (Fernández-

Martínez et.al., 2015). Through bioaccumulation, methyl mercury concentrations increase through the food web with the highest concentrations in large fish and wild animals. Total mercury concentrations from Pinchi soils still exceeded CRS industrial standard (150 mg/kg for toxicity to soil invertebrates) in some sites from 2004-2007. (Figure 9).

As the distance from the mine increases, Hg concentration on surface soil decreases and reached no more than 10km from the mine, with the old operation sites having a much higher concentration, and the majority of the concentrations are within a 2-5 km radius (Fernández-Martínez et.al., 2015; Allard et.al., 2013). The total concentration includes free Hg (0), matrix-bound Hg, and available Hg in soils. Among the three, matrix-bound Hg is the most important Hg phase as it accounts for Hg complexed to soil components. Matrix-bound Hg is formed during the roasting process and adsorbed to other organic and inorganic components. When matrix-bound Hg is further methylated or oxidized to reactive Hg(II), it becomes more mobile and more bioavailable (Gray et al., 2004). Hg becomes desorbed at higher pH values, and desorption of Hg (II) is stronger when Zn (II) when present (Jing et al., 2007).

Remediation

Ecological Risk Assessment (2004-2009) (ERA) was used to guide management decisions for the closure of the Pinchi mercury mine. Focused areas included the Pinchi Lake shoreline, a tailings Impoundment area on the eastern portion of the mine site, both old and modern mills, two open pits, three waste rock piles, four accessible mine adits, and portals, and several old-growth forested sites (Allard et.al., 2014). An initial step of an ERA is problem formulation. Surveys were carried out to identify and analyze potential risks and concerns of contaminants, and the major wildlife receptors. The results suggested that the methyl mercury level was negligible for most of the species in the region. However, because the samples were collected mostly from topsoil, contamination of air and water, and the associated health risks to humans and wildlife were underestimated. The same measures were taken in the “Decommissioning and Remediation of the Pinchi Lake Mine” (Donald et.al., 12013). The report identified elevated mercury levels mostly in insects and small mammals but neglected future potential for bioaccumulation.

Long-term monitoring by Teck Resources evaluated the effectiveness of the closure plan and the initial two-year remediation plans (Unger et.al., 2013). The monitoring plan covers Ecological Risk Assessment; Environmental Site Assessment, Human Health Risk Assessment, Re-vegetation Plan, and Geotechnical Monitoring. The factor of residual risk was added for consideration. Territorial monitoring and water quality monitoring were planned to be conducted for at least three years. A ten-year period was given from 2012 to give vegetation sufficient time to develop a deep enough root system to penetrate through contaminated soils. Extensive monitoring on mercury levels in fish species, including trout in the Lake and two surrounding lakes, Tezzeron Lake and Stuart Lake, was limited This full suite of monitoring on limnology, water chemistry, sediment chemistry, zooplankton, and benthic invertebrate community structure and mercury concentrations, and various fish species was expected to to continue for at least ten years. In addition, Wilson Scientific Consulting Inc. (Wilson Scientific) completed a Human Health Risk Assessment (HHRA) of the chemical exposure (Wilson Scientific, 2010). To ensure the result of HHRA is still valid, it will be necessary for the site to continually be properly managed.

Remediation Recommendations and Future Directions

My study shows clearly that each mine has different features. Therefore, there cannot be one solution to all of the mines. The BC Reclamation Act requires that the mining company develop a reclamation program and posting of a reclamation bond, to ensure that when a mine has" reached the end of its purposeful life, the land is restored to its former (or an acceptable) condition, and the monitoring necessary as per the reclamation plan is completed" (Construction Bond, 2022). The analysis of remediation actions of each case in this project shows that reclamation should not be left to the latter part of the mining operation but should be initiated at the exploration stage by establishing protocols and monitoring. For the production of potential hazards such as heavy metals.

Basic information may be obtained by reports about regional geology and directions of remediation. To make the mine site adapt to the ecosystem, bioremediation with a minimum

Each mine has unique problems such as a lack of appropriate microbiomes. Characterization of mine sites and the literature aids in processes such as large-scale fertilization.

Bioremediation with microbes with a focus on SRB

Recently, there has been an increase in studies focused on the bioremediation of AMD (Table 1). The use of sulfate-reducing bacteria (SRB) iron-reducing bacteria (IRB), mycorrhizae fungi remediation, and phytoremediation. These are particularly interesting because of their energy efficiency. Chemical remediation usually has low efficiency in heavy-metal reduction, and compared with iron-exchange remediation methods such as enhanced electrokinetic remediation for contaminated soil, bioremediation requires less energy input and financial costs and as well adds nutrients to the soil (Bryan, Hallberg and Johnson, 2006). Additionally, bioremediation methods can often act synergistically and improve soil health and ecosystem function. For example, adding rhizobacteria and mycorrhizal fungi into the soil can create better soil to support tree seedlings (Li et.al., 2021).

Microbial activity can solubilize and/or precipitate metals through metabolic processes, change the pH or redox conditions, secret chelating agents and organic acids, and/or through passive sorption. However, the geochemical properties such as pH, temperature, and elements in soil have direct effects on microbial communities and their diversity, as well as vegetation composition. Further knowledge and control of the different biological processes promoting precipitation, sorption, and redissolution of metals in different conditions are required to find the best approach to implement bioremediation for AMD.

Sulfate-reducing bacteria (SRB) are widely used in AMD remediation because of their ability to produce acid streams (biofilm) in mine waters. SRB utilize sulfate as the terminal electron acceptor for the metabolism of organic substrates under anaerobic conditions. During the process, SRB generate energy with necessary nutrients provided by external organic matter and necessary electron acceptors.

It is common for SRB to use multiple metabolic pathways to function in different environments. During the energy-acquiring process, they precipitate heavy metals and reduce metals' solubility. The reaction can be described in functions (1) and (2).

(3) $SO_4^{2-} (aq) + 10H^+ (aq) + 8e^- \rightarrow H_2S (aq) + 4H_2O (l)$

Iron was oxidized in the process

(4) $4Fe(s) \rightarrow 4Fe^{2+} (aq) + 8e^-$

The ferrous iron then reacts with either OH- ions or sulfide ion to form insoluble iron compounds. These bacteria particles can be clumped together to form larger clumps called rusticles.

Table 1Sulfate-reducing bacteria in AMD remediation.

Isolate	**Source of mine waste**	**Amendment added**	**Original pH**	**Sulfate removed (%)**	**Metals removed**	**Reference**
SRB including *Desulfosporosinus Orientis*	Synthetic Carnoulès AMD	glycerol	4	-	As, Zn, Fe	La Pape, et.al, 2017
SRB collected from activated anaerobic sludge of a wastewater treatment plant	Copper AMD Sludge	Fe0 (Iron powder)	7	100	Cu	Bai et.al, 2013 (2)
Consortium of Acidophiles	São Domingos Copper mine tailings	-	2.29	-	Cu, Fe, Zn	Bryan et.al., 2006
Desulfovibrio desulfuricans and Desulfomicrobium baculatum	Synthetic mine waste	Ethanol	3–4	90	As, Cu, Fe, Ni, Zn	Sahinkaya et al., 2015
Sulfate-reducing bacteria	Synthetic acid mine drainage	Chicken manure Dairy manure Sawdust	3.0–3.5	79.04, 64.78 50.27,	Cd, Cu, Fe, Mn, Ni, Zn	Zhang and Wang, 2014
SRB and IRB include esulfosporosinus sp., Syntrophobacter sp., Acidiphilium sp., Acidobacterium sp., Acidosphaera sp., Acidithiobacillus ferrooxidans, Thermoplasmata, Chlorella sp., Zygnematales	AMD water from La-Zarza-Perrunal Gold and silver mines	-	3.1	-	Fe, Al, Ca, Cd, Cu, Zn, Ni, Co, As, Pb	Gonzalez-Toril et al. (2011)

Immobilized sulfate-reducing bacteria sludge granules	Synthetic acid mine drainage	Lactate	2.8 7.8-8.3	80.2 99%	Cd, Cu, Fe, Mn, Zn	Zhang and Wang, 2016
enriched from sediments of the acidic mine pit lake 111 situated in the Lusatian lignite mining district in Brandenburg, Germany.	Mimicked AMD	H2/CO2 as carbon source/electron donor	3.3, 3.8, 4.8, and 5.9	reduction rates were 8.6, 6.6, 12.7, and 17.7 fmol sulfate /cell/day corresponding to pH	Fe, Zn, Cu	Meier et.al., 2011
Sulfate-reducing bacteria	Synthetic wastewater and acid mine from copper mine	Lactate, iron	2.75	61	Cu, Fe, Mn	Bai et al., 2013 (1)
A consortium of sulfate-reducing bacteria	Synthetic wastewater	-	6.0	67	Cu, Cr, Ni, Zn	Kieu et al., 2011
SRB and IRB: Desulfosporosinus, Desulfitobacterium, Desulfotomaculum, Alicyclobacillus, and A. ferrooxidan	Mimicked AMD by adding pyrite and salt	Sodium Lactate, Yeast Extract	~5	44	Fe	Jing et.al., 2017
SRB including Desulfobulbus (~11%)	Main tailing water from two historic mine sites in Sonora, Mexico	Lactate	3.67-6.58	~100	As, Pb, Cd, Co, Cr, Cu, Mn, Sr, and Zn	Valenzuela et.al., 2020

Factors affecting sulfate-reducing efficiency---pH, amendment, and metal type

The sulfate-reducing rates differ greatly among the reported studies. Many factors explain the variance. Factors such as incubation time, initial temperature, pH, and the metal type all affect how microbial communities co-exist and precipitate the metal and amendments added, as well as procedural differences including how bioreactors were adjusted and the rate of sulfate loading (Bai et.al., 2013 (2)).

The initial pH ranges from 2.29 (Bryan et.al., 2006) to 7 (Bai et.al, 2013 (1)). Most SRB grow optimally between pH 6 and 8, with some acidophile SRB that can function at a pH around 3 (Ayangbenro et.al., 2018). It appears among the studies that pH does not overshadow the effects of amendments added. The most effective cases (Valenzuela et.al., 2020, Sahinkaya et al., 2015) do not have the optimal pH for SRB but most have some form of amendments. Zhang and Wang, (2016) study achieved an 80% sulfate-reducing rate with a pH of 2.8. With pH changing from 2.8 to 7.8/8.2, the removal rates of metals rate increased to 99%. The introduction of acid-tolerant SRB can enhance the remediation performance of metal recovery in new bioreactor systems. Most SRB species are mesophilic, but SRB also includes some thermophilic and psychrophilic species. Temperature affects the activity of SRB, but because of the diverse composition used by different studies, it is difficult to determine exactly how temperature changes affect metal uptake rates. Bai et.al. (2013 (2)) found that SRB needs a longer time to adapt to low-temperature environments. The sulfate reduction rate of SRB was 90%, 85%, and 67% at 28, 25, and 22 C. When Iron powder was added, the removal rate improved to 95% throughout a fairly common temperature range. This proved that SRB's effectiveness in mining remediation can be highly variable at different sites and at different seasons.

Lactate can inhibit the growth of iron-oxidizers but cannot stop the oxidization of pyrite (Valenzuela et.al., 2020). Whereas organic matter can alter the microbial community and stop pyrite oxidation (Jing et al., 2018, Valenzuela et al., 2020). By the addition of an external source of electron donors (hydrogen, acetate, lactate, etc.) controlling the oxidizing environment, the process of SRB reducing metals and using the reduced metals as electron acceptors can be accelerated. The addition of water-retaining agents and mineral-solubilizing microbes into the soil can augment the root-reinforced soil shear strength, as well as the root tensile force and tensile strength. Mineral-solubilizing microbes' ability to assist root development was enhanced by water-retaining agents. The microbes did not improve soil pH without the water-retaining agents but ameliorated total soil carbon, total nitrogen, total sulfur, and available phosphorous. Although the addition of water-retaining agents decreases root diameter, it increased the root length, surface area, and volume. The decrease in root diameter can be translated as root elongating and densifying (Li et.al., 2020). By enhancing root-induced soil shear strength, mineral-solubilizing microbes and water-retaining agents demonstrated an important role in slope stability. These findings are valuable for remediation on steep slopes and semi-arid regions.

Due to the complex nature of AMD wastewater, there is no single-metal analysis reported in different studies. Several iconic toxic heavy metals include mercury, arsenic, copper, and cadmium. SRB As (V) is less mobile than As (III) and can strongly sorb to iron (III). Ferric iron is enzymatically reduced to ferrous iron which acts as an electron acceptor, and As (V) in these situations becomes aqueous. Therefore, microbial reduction of As (V) would lead to increased mobility of arsenic in water, when there are sufficient electron donors and limited oxygen transfer (Newsome and Falagán, 2021). As (III) can then become incorporated into iron sulfide minerals, given the sufficient reducing environment that usually happens in mine tailings. As can be precipitated from solution to sulfide minerals coupled to oxidation of organics such as ethanol or lactate, via bacterial activities (Zhang, Moon, Myneni, and Jaffé, 2017). With added glycerol in the solution, SRB was able to precipitate 73–87% As as orpiment (As2S3) and realgar (As4S4), and 18–28% of Zn during the first 14 days, and accomplished a full removal (metal concentration below detected limit) of As and Zinc in 94 days (Le Pape et.al., 2017).

There is no effective case showing mercury remediation due to its toxicity in different forms and unstable reaction with microbes. Mercury is particularly toxic and can occur with other heavy metals such as As. A high concentration of mercury in the soil can alter the microorganism's community and change it into more Hg-resistant groups (Lello et al., 2010). Additionally, mercury adsorption by the soil is highly pH-dependent as it becomes desorbed at higher pH values. The organic form of mercury is methylmercury, and the process of methylation of mercury is mostly undertaken by SRB. The high solubility and mobility of methylmercury make it difficult to stabilize, and it can be bioaccumulated in fish and human bodies (Donald et al., 2013). The process of Hg (II) being methylated and the methylated Hg then can diffuse out from a membrane is considered the major Hg resistant mechanism (Schaefer et al., 2014). Demethylation of methylmercury to Hg (II) and CH_4 is dominated by some other strains of bacteria as well. Which process should be considered a detoxification process is debatable. In remediation practices, simply adding SRB consortium would generate more volatile Hg0 which can lead to more environmental problems. Or, SRB can generate highly soluble and mobile methylmercury which causes water pollution. This could explain why there is no reported Hg in the remediation cases.

Synergistic Effects of Engineered Consortia to Improve Bioremediation Efficiency

One of the largest limitations of SRB is its sensitivity to low pH. This can limit its application in some highly acidic mine tailings without other amendments. Under the same treatment and in the same environment, an increase in pH directly corresponds to a decrease in sulfate-removal efficiency (Table 1). In a study by Meier et.al.,(2011), the initial pH for wastewater enrichments was set to approximately 3 – 6, they found that the increase in pH was concomitant to a decrease in sulfate.

Another potential drawback of SRB that could prevent its wide application is its reliance on amendments. Almost all the studies relied on external carbon source/electron donors and nutrient sources. SRB often require energy from the process of lactate reduction to acetate. In other studies, a zero-valent iron supplement was applied as an electron donor to enhance SRB's performance. They can both be used as materials for permeable reactive barriers (PRBs) utilized in heavy metal capture. In some other cases, manure and other biomass were added with SRB (Jing et al., 2018). This adds a step for remediation planning. The cost and continuity of biomass become important, as well as the organic matter's biodegradability and availability. To plan for more sustainable remediation, how organic matter would affect soil quality and whether the constructed soil would match its native environment requires further monitoring.

Furthermore, SRB functions in anaerobic conditions, which would be acceptable in most cases in mine tailings remediation. However, as soon as they are exposed to air, the remediation functions can be lost. While in many cases the remediation plan's end goal is a constructed wetland, some end land use goals may require elevation lift of land to create a more aerobic condition in soil for plant growth.

Overall, SRB, along with any other bioremediation techniques, has a high variability of effectiveness as shown in Table 1. Temperature, level of dissolved oxygen, organic matter, water level, the presence of iron, source of carbon, and most importantly the concentration of sulfates can all affect the physiological state of SRB, thus impacting their metal tolerance. The different compositions of metals in different mines and how they interact can also affect SRB's survival rates and consequentially their ability to precipitate or stabilize the metals.

Future directions of SRB remediation

While implementing microbial remediation, it is important to perform a comprehensive analysis of site conditions. Factors like soil pH, for example, can affect the choice of microbes used. Metal contaminants and high acidity in mine sites cause damage to the environment as well as human health on a global scale. Microbes such as SRB have a range of mechanisms to utilize the excessive sulfate and survive extreme environments. SRB is very effective tools for AMD remediation in many different environments by transferring metals through aqueous and solid forms or methylated and demethylated forms. However, nutrients and carbon sources are required for SRB's maximized effects. Engineered microbial consortia show a more robust reaction toward environmental fluctuations. In Nature, microbial consortia exist to fill different roles including forming biofilms (Keller et al., 2006). By selecting certain consortia for better performance or desired properties in remediation, humans can improve the results of remediation or accelerate the results. Eukaryotic organisms, such as algae and fungi that can tolerate higher acidity and heavy metal concentration could be engineered with SRB (Brune and Bayer, 2012). In fungi-driven AMD, excess Zn can be sequestered in the vacuole and bound to polyphosphates (Wei et.al., 2013). Fungi can also bioaccumulate Hg in their bodies, solving the dilemma created by SRB of whether Hg0 pollutes the air or Hg2+ pollutes the water. The use of tailored viruses and bacteriophages can improve the formation of biofilms that prevent the attachment of iron-oxidizers. In general, the ability to manipulate microbiome composition for remediation would create more opportunities to rely less on abiotic chemicals and improve metal recovery, as well as improve soil quality. Despite the limitations of using SRB, many biotic and abiotic amendments can be constructed into the remediation planning.

Conclusion

Based on the cases, it is clear that mining activities have a significant impact on surrounding environments. The effects of metals are largely dependent on the type of major metals and their geochemical and biochemical behavior. Geological conditions including rock type, elevation, slopes, surface, and groundwater networks all have impacts on the overall mining impacts. Certain geological characteristics combined with regional climate can aggravate or mitigate leaching and AMD problems, and influence decision-making for remediation plans.

The current remediation plans are moving to include a more comprehensive view to allow a more comprehensive plan to restore ecological functions, protect and maintain acceptable habitats for wildlife, and benefit the health and well-being of local communities. However, remediation based on a true cumulative effects protocol, even though the Government of BC is committed to considering cumulative effects in natural resource decision-making, is still lacking Improving cumulative effects assessment and management is a vital part of sustainable and integrated resource management (Province of British Columbia, 2022). To ensure the results of remediation, a set of policies and procedures should be developed to inform decision-makers to enable consistent, coordinated, and comprehensive management.

Recommendations

Before any activity begins to activate mining operation, there should be a comprehensive assessment of the geological properties of the ore body and the local ecosystems including the climate, land, and water resources of the affected area of the proposed mine.

The second recommendation is that a flexible reclamation plan is provided along with the application for approval by the Government.

As suggested the reclamation plan should be flexible to address unexpected emergent outcomes during the mine's operations. Important parameters such as water quality should be closely monitored, and regular surveys should be conducted as the operation goes.

More research, on-site, is required to assess and implement the utility of biofertilizers and adapting microbiomes for successful reclamation. For example, how to apply microbiome into mine waste to neutralize and detoxify in a large scale would be beneficial for future practices.

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