

Evaluation of the Potential Impacts of Submerging the Oxidized Tailings and Adding a Cover Layer at Mine Principale

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Statement of Contributions

There are a number of co-authors on this thesis. As the principal author on each paper, I took a lead role in collecting sampled cores in the field, cutting cores and extracting samples, analyzing data, and writing chapters. The following summarizes the contributions of co-authors.

Chapter 1: This chapter was written solely by Majak Agau. Carol Ptacek, David Blowes, Isabelle Demers, and Jenine McCutcheon provided feedback on the chapter.

Chapter 2: This chapter was written by Majak Agau and Eva Pakostova. Eva Pakostova authored the microbiological section, while Majak authored the rest of the chapter. Carol Ptacek, David Blowes, and Jenine McCutcheon provided feedback on this chapter.

Chapter 3: Majak Agau wrote this chapter. Carol Ptacek and Isabelle Demers provided feedback on the chapter.

Abstract

Oxidation of sulfide minerals generates acid and forms various secondary phases including Fe(III) (oxy)hydroxide phases, jarosite, and gypsum, which can attenuate hazardous metal(loid)s by precipitation, co-precipitation, and adsorption reactions within tailings. The abandoned Cu-Ag mine at Mine Principale, Chibougamau, Québec, has three tailings impoundments (Parcs, A, B, and C) that have oxidized for more than 50 years. This project focused on Parc B, where tailings are stored to an average depth of 8.0 meters below the ground surface (mbgs). The study involved mineralogical, chemical, and microbiological analyses to evaluate the potential impacts of the proposed elevated water table (EWT) technique on the partially oxidized tailings. The EWT involves raising the water table and maintaining it above reactive tailings. Increasing the water content limits sulfide-mineral oxidation by minimizing O₂ ingress into the tailings, owing to its low diffusivity in saturated media. However, the EWT can cause direct dissolution of soluble secondary phases, and also can potentially induce reducing conditions that promote microbially catalyzed reductive dissolution of Fe(III) (oxy)hydroxide phases fueled by organic C compounds. In this study, mineralogical and selective chemical extraction techniques indicate the presence of various secondary phases including Fe(III) (oxy)hydroxides that are associated with significant amounts of hazardous metal(loid)s including Cu, Ni, Co, Zn, As and Pb in the oxidized zone, which is limited to a depth of about 1.5 mbgs in Parc B. Results of amplicon sequencing of 16S rRNA genes show significant abundances of Fe- and S-oxidizing bacteria and S-reducing bacteria but no presence of Fe-reducing bacteria. Solid-phase analyses indicate a low amount of total C in the oxidized tailings. These findings suggest that EWT technique can be an effective reclamation method for Mine Principale tailings if use in conjunction with another suitable method to address potential low-quality drainage resulting from the inducement of reducing conditions post EWT application.

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Dedication

This thesis is dedicated to my always loving parents, Agau Majak and Akur Kelei, for their support and continuous belief in me. Most importantly, I would like to express my sincere gratitude to my lovely wife, Akon Awuou, for her unwavering support, love, and encouragement throughout this academic journey.

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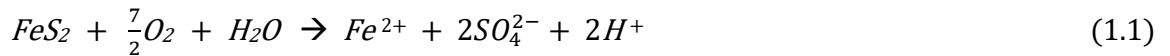
Chapter 1: Introduction

1.1 Background

1.1.1 Mine Wastes and Sulfide-mineral Oxidation

Mining of metals generates the largest volume of waste in the world (Blowes et al., 2014). In Canada alone, the amount of waste generated by the mining industry is more than 20 times the amount of all municipal solid wastes produced each year (MiningWatch Canada, 2003), with waste rock and mine tailings being the main contributors (Blowes et al., 2014). Waste rock is the rock excavated to reach the ore in open-pit, strip, or underground mines. Mine tailings are a by-product of the mining process, which are often created when ore deposits are crushed, ground into fine-grain size particles of about 0.025 - 1.0 mm. Water and surfactants are usually added to tailings to promote separation of valuable minerals from gangue materials, including sulfide minerals. Exposure of sulfide-rich mine wastes to atmospheric oxygen (O₂), in the presence of water, can lead to the generation of a low-quality drainage characterized by elevated concentrations of Fe, SO₄, and other dissolved metal(loid)s (Moncur et al., 2006; Nordstrom et al., 2015).

Pyrite [FeS₂] is the most common sulfide mineral in most mine tailings impoundments (Rimstidt & Vaughan, 2003; Blowes et al., 2014, Nordstrom et al., 2015). The oxidation of pyrite occurs when grain surfaces are exposed to oxidants such as O₂ and Fe(III). The oxidation of pyrite by O₂ produces 1 mole of Fe(II), 2 moles of SO₄ and 2 moles of H⁺ for every mole of pyrite oxidized (Nordstrom, 1982):



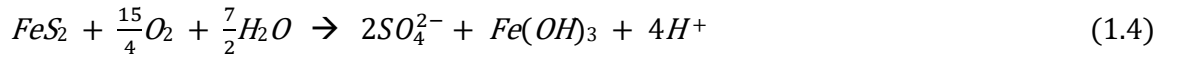
Trace elements associated with pyrite including As, Pb, Cu, Co, Ni, Zn, Au, Ag, Sb, Bi, Se, and Te, may also be liberated during the oxidation of pyrite (Deditius et al., 2011; Nyström et al., 2019). In the presence of excess O₂, the Fe(II) shown in reaction (1.1) can be further oxidized to Fe(III):



At pH > 5, Fe(III) hydrolyzes to form precipitates of Fe(III) (oxy)hydroxide, such as goethite [α -FeOOH] and ferrihydrite [$5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$], generating additional H^+ (Janzen et al., 2000) through:

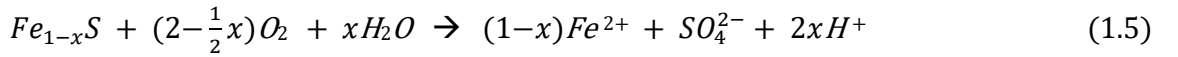


where $\text{Fe}(\text{OH})_3$ is representative of a range of Fe(III) (oxy)hydroxide phases. Although 1 mole of H^+ is consumed in the oxidation of Fe(II), 3 moles of H^+ are produced in the hydrolysis of Fe(III) and subsequent precipitation of Fe(III) (oxy)hydroxide phases. Addition of reactions (1.1), (1.2), and (1.3) yields the overall reaction:

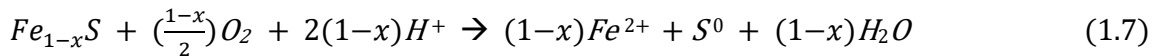
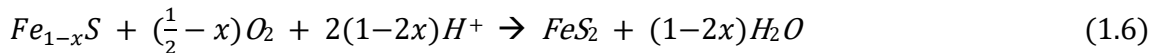


In this overall reaction (1.4), 2 moles of SO_4 , 4 moles of H^+ , and 1 mole of Fe(III) (oxy)hydroxide precipitates are produced for 1 mole of pyrite oxidized by O_2 .

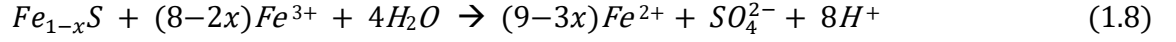
Pyrrhotite [Fe_{1-x}S] is the second most common sulfide mineral in sulfide-bearing wastes (Nordstrom et al., 2015). The crystal lattice of pyrrhotite has Fe vacancies that can be charged compensated by Fe(III) (Murphy & Strongin, 2009). The dissolution of pyrrhotite occurs in oxidative and non-oxidative pathways (Thomas et al., 1998). The oxidative dissolution of pyrrhotite by dissolved O_2 proceeds (Janzen et al., 2000) as:



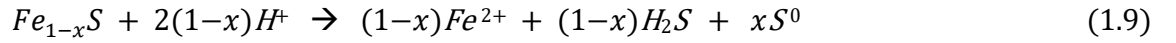
Similar to pyrite, pyrrhotite hosts trace metals such as Ni and Co (Gunsinger et al., 2006; Cameron et al., 2021), and can release these trace metals, together with Fe, upon oxidation. The amounts of Fe(II) and H^+ released in reaction (1.5) is dependent on iron content and the amount of O_2 present in the tailings (Lindsay et al., 2015). Partial oxidation of pyrrhotite can result in the formation of secondary alteration rims of marcasite [FeS_2] and elemental sulfur [S^0] (Janzen et al., 2000):



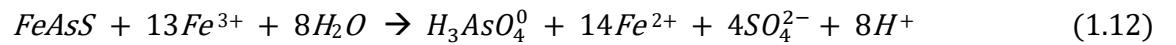
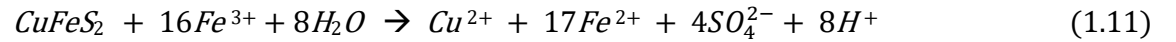
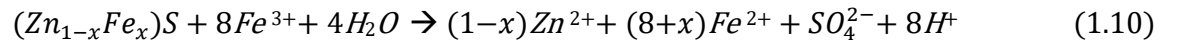
The formation of marcasite and elemental sulfur limits the formation of sulfate (Blowes et al., 2014) and reduces oxidation rates (Moncur et al., 2009). The presence of Fe(III) in pyrrhotite has been observed to expedite the oxidation of Fe(II) to Fe(III), and, therefore, accelerates the overall oxidation of pyrrhotite by Fe(III) (Moncur et al., 2009):



The oxidation of pyrrhotite by Fe(III) is more rapid than by O₂ (Thomas et al., 1998). According to Chiriță & Rimstidt (2014), non-oxidative dissolution of pyrrhotite, in acidic conditions, can result in the formation of Fe(II), H₂S, and S⁰:



In addition to pyrite and pyrrhotite, other sulfide minerals including sphalerite [(Zn_(1-x)Fe_x)S], chalcopyrite [CuFeS₂], pentlandite [(Fe,Ni)₉S₈], and arsenopyrite [FeAsS] can also contribute to the generation of low-quality drainage by releasing Fe, SO₄, Zn, Cu, Ni, As, H⁺, and other associated metal(loid)s through the oxidation by O₂ and Fe(III). For instance, Fe(III) usually generated in acidic solutions by the oxidation of pyrite and pyrrhotite can promote the oxidative dissolution of sphalerite, chalcopyrite, and arsenopyrite, liberating SO₄, Zn, Cu, As, Fe(II), and H⁺ in the process (Rimstidt et al., 1994):

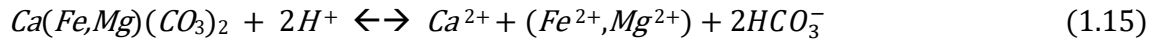
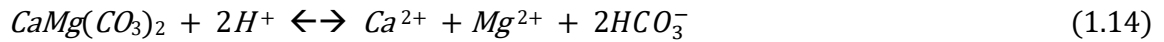


Oxidation of sulfide minerals can also be catalyzed by acidophilic microorganisms. Sulfide minerals that dissolve in acid, like sphalerite, can be oxidized by bacteria such as *Acidithiobacillus thiooxidans* that oxidize elemental sulfur and reduced inorganic sulfur compounds to sulfuric acid. Contrarily, acid-insoluble sulfide minerals are stable in acidic solutions of sulfuric acid but are susceptible to oxidative dissolution. In acidic solutions, Fe(III) serves as a more significant oxidizing agent for sulfide minerals compared to O₂,

and as a result, bacteria like *Leptospirillum* spp., which oxidize Fe(II) to Fe(III), become the primary agents responsible for the oxidation of acid-insoluble sulfide minerals (Blowes et al., 2014).

1.1.2 Acid Neutralization

Gangue minerals present in mine wastes can neutralize H^+ release by the oxidation of sulfide minerals. The gangue minerals that contribute to acid-neutralization reactions include carbonates, oxyhydroxides, and aluminosilicate minerals (Jambor et al., 2002). The successive dissolution of these gangue minerals results in a sequence of pH-buffering zones (Blowes and Ptacek, 1994; Blowes et al., 2014). The equilibrium dissolution of primary carbonates such as calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$], and ankerite [$Ca(Fe,Mg)(CO_3)_2$] maintains the pore-water pH near circumneutral conditions (pH 6.5 - 7.5) (Jurjovec et al., 2004) through:



The dissolution of primary carbonates consumes H^+ and releases metals (e.g., Ca, Mg, Fe) and HCO_3^- as by-products (Blowes et al., 1998). The acid-neutralization capacity of carbonates depends on their abundance and reactivity (Strömberg & Banwart, 1999; Lindsay et al., 2015).

During the dissolution of primary carbonates, precipitation of siderite, $Al(OH)_3$, and $Fe(OH)_3$ is favoured (Blowes et al., 1994). Ferrous iron released via sulfide-mineral oxidation can react with calcite to form siderite (Al et al., 2000; Jurjovec et al., 2002) through:



or can react with HCO_3^- generated from the dissolution of primary carbonates to form secondary siderite (Morin and Cherry 1986; Ptacek and Blowes 1994). The depletion of primary carbonates results in an abrupt decline in pore-water pH, which can be moderated by the dissolution of primary siderite originally present in

the gangue materials or secondary siderite accumulated during the dissolution of primary carbonates (Blowes et al., 1994; Jurjovec et al., 2002):



As carbonate minerals dissolve, the most soluble aluminosilicate minerals, such as biotite, may release dissolved Al to the pore-water (Murakami et al., 2003), where it may precipitate as gibbsite $[Al(OH)_3]$ or another Al oxyhydroxide mineral phase:



This dissolution (reaction 1.16) buffers the pH to values between 4.8 and 6.3 (Blowes et al., 1994), sequestering 2 moles of H^+ while producing Fe(II) and bicarbonate. The Fe(II) liberated can be oxidized in surface water bodies, generating 3 moles of H^+ per 1 mole of siderite. As a result, the dissolution of secondary siderite does not contribute to a net increase in acid neutralization capacity (Lindsay et al., 2015).

When siderite is completely consumed, the pH declines sharply, and $Al(OH)_3$ becomes the next pH buffer. Dissolution of $Al(OH)_3$ maintains the pH to values between 4.0 and 4.3. The pH declines once $Al(OH)_3$ is totally depleted, favouring the dissolution of $Fe(OH)_3$, which maintains the pore-water pH between 2.5 and < 3.5 (Blowes et al., 1994, Gunsinger et al., 2006). The dissolution of $Al(OH)_3$ and $Fe(OH)_3$ consumes H^+ and release either Fe^{3+} or Al^{3+} (Lindsay et al., 2015) through:



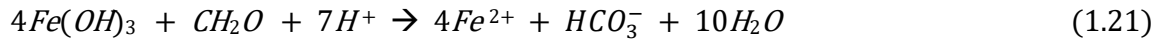
The pore-water within zones of oxyhydroxide dissolution is characterized by pH values ranging from approximately 2.5 to 4, along with elevated concentrations of dissolved Al and Fe(III) (Lindsay et al., 2015).

After the depletion of carbonate minerals and Al and Fe(III) hydroxides in the tailings, the dissolution of aluminosilicate minerals becomes the dominant process contributing to acid neutralization (Blowes et al., 2014). Since the dissolution rate of aluminosilicate minerals is relatively slow compared to

the flow of groundwater, water systems at some abandoned mine sites can produced waters with pH values < 1 (Nordstrom et al., 2000, Moncur et al., 2005).

1.1.3 Reduction of Ferric Iron and Sulfate

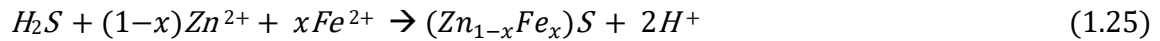
The microbially mediated reduction of Fe(III) to Fe(II) in Fe(III) (oxy)hydroxide phases, which results from the oxidation of sulfide minerals, can promote the remobilization of associated metal(loid)s in anoxic environments (Ribet et al., 1995):



The remobilized metal(loid)s, however, can be attenuated via microbially mediated SO_4 reduction, which releases H_2S and HCO_3^- (Hulshof et al., 2003; Moncur et al., 2006) through the reaction:



where CH_2O denotes a generic organic compound. The formation of H_2S in the presence of high concentration of dissolved metal(loid)s such as Fe, Cu, and Zn can promote the precipitation of secondary metal sulfides such as mackinawite $[FeS]$, covellite $[CuS]$, and sphalerite $[Zn_{(1-x)}Fe_x]$ (Moncur et al., 2006):



These secondary sulfide precipitates are important sinks for Fe, Cu, Zn, and other metal(loid)s because they exhibit low solubility in sulfide forms (Lindsay et al., 2015). The microbially catalyzed reactions, (1.21) and (1.22), occur more rapidly in the presence of organic compounds (Ribet et al., 1995). Organic compounds such as acetate and lactate can be provided by acid-producing (fermentative) bacteria through the fermentation of complex organic substrates (Lovley & Phillips, 1989; Hulshof et al., 2003).

The oxidation of sulfide minerals results in the generation of acid and formation of various secondary phases including Fe and Al oxyhydroxides, jarosite, covellite, marcasite, and gypsum, which largely attenuate metal(loid)s by precipitation, co-precipitation, and adsorption reactions within the tailings

(McGregor et al., 1998; DeSisto et al., 2011). Under changing geochemical conditions such as the inducement of reducing conditions in the form of a cover system, toxic metal(loid)s associated with secondary Fe(III) (oxy)hydroxide phases, nevertheless, can be remobilized for years to decades via reductive dissolution reactions (Gunsinger et al., 2006).

1.1.4 Controls on Sulfide-mineral Oxidation

Sulfide-mineral oxidation can be controlled by limiting the amount of oxygen interacting with sulfidic wastes and inhibiting the growth of oxidizing microorganisms in abandoned mine sites. The most widely used O_{2(g)} transport barriers include water covers (Awoh et al., 2013; Moncur et al., 2015), which limit O₂ transport due to its low diffusion coefficient in a layer of water (Mbonimpa et al., 2003; Adu-Wusu & Yanful, 2006), covers with capillary barrier effect composed of materials that maintain high degrees of saturation and low gas-phase diffusivities (Bussière et al., 2003; Dagenais et al., 2005; Kalonji et al., 2017), barrier-type covers made of materials with low O₂ diffusivities (Lundgren, 2001), covers composed of oxygen-consuming materials (Tassé et al., 1994; Peppas et al., 2000), and covers designed to promote an elevated water table that also take advantage of the low diffusion coefficient of O₂ in saturated or nearly saturated porous media (Dagenais et al., 2006; Ouangrawa et al., 2010; Maqsoud et al., 2019). Bacterial activity is inhibited by the application of bactericides, most notably anionic surfactants (Blowes et al., 2014).

1.1.4.1 Water Covers

Water covers rely on the low solubility (8-13 mg/L) and diffusivity ($2.0 \times 10^{-9} \text{ m}^2/\text{s}$) of O₂, at normal surficial temperatures, through a water layer to limit the rate of sulfide-mineral oxidation (Mbonimpa et al., 2003; Adu-Wusu & Yanful, 2006; Blowes et al., 2014). This is achieved by depositing the reactive mine wastes in natural water bodies such as lakes or marine systems, or in engineered impoundments designed to maintain the water cover (Blowes et al., 2014). Moncur et al. (2015), for example, examined the long-term mineralogical and geochemical evolution of sulfide mine tailings exposed to two types of weathering conditions for over 50 years: (1) sub-aerial tailings subjected to atmospheric conditions, and (2) sub-aqueous

tailings stored under a 100 cm deep water cover. Mineralogical characterization of sample cores collected from sub-aerial tailings and sub-aqueous tailings showed that the extent of sulfide-mineral oxidation in sub-aerial tailings was more extensive and the oxidation zone extended from the surface to a depth of about 40 cm, whereas sub-aqueous tailings had mild oxidation and the oxidation zone was restricted to 6 cm below the water-tailings interface. Additionally, pore-water collected from sub-aerial tailings exhibited low pH conditions (pH 1.9 - 4.43), and elevated concentrations of dissolved S (7900 - 59000 mg/L) and Fe (3500 - 28000 mg/L) while those obtained from sub-aqueous tailings showed circumneutral conditions (pH 7 - 7.15), and relatively lower concentrations of dissolved Fe (0.16 - 1.35 mg/L) and S (1600 - 1700 mg/L). These results suggest that sub-aqueous disposal of reactive mine tailings is a suitable approach for limiting the formation of AMD. Due to environmental risks that may result from the disposal of mine wastes in natural water bodies, mining companies considering sub-aqueous disposal usually face regulatory barriers (Blowes et al., 2014). Mine sites may also be located in remote places where there are no water bodies capable of containing the entire mine wastes. In these scenarios, design of surface depositories with adequate capacity to maintain water covers has been carried out (Davé & Vivyurka, 1994). These surface depositories, however, have significant dyke stability issues, are expensive and may be difficult to maintain in the long term (Ouangrawa et al., 2010). Tailings resuspension by wind and wave action, and potential production of O₂ by periphyton on the tailings surface are other issues associated with sub-aqueous disposal of reactive mine tailings (Yanful & Verma, 1999; Vigneault et al., 2001).

1.1.4.2 Covers with Capillary Barrier Effect (CCBE)

Covers with capillary barrier effect depend on the moisture-retaining properties of fine-grained materials to maintain one (or more) of its layers near saturation at all times (Nicholson et al., 1989). They function based on a capillary break phenomenon that occurs under unsaturated conditions when a fine-grained material overlies a coarse-grained one. The contrasting differences in hydraulic properties between the two materials restrict downward flow of water since the coarse-grained material is easily drained and, therefore, shows a much lower unsaturated hydraulic conductivity than the overlying fine-grained material that has a superior water retention capacity (Aubertin et al., 2009). This restriction on the downward flow of water helps maintain a high degree of saturation in the fine-grained material, reducing the influx of O₂. By limiting O₂ diffusion into the reactive tailings, the highly saturated fine-grained material effectively limits the generation of AMD (Bussière et al., 2003). A typical CCBE cover system consists of 3 - 5 layers. In a five-layered CCBE (Figure 1.1), the bottom layer is made of a coarse-grained material used both as mechanical support and as a capillary break. The fine-grained moisture retaining layer is placed over the coarse-grained material to create the capillary barrier effect. The second coarse-grained material is placed over the moisture retaining layer to prevent water loss by evaporation and to facilitate lateral drainage. The protection and surface layers are used to prevent erosion and bio-intrusion (Bussière et al., 2003). Application of CCBEs can be carried out on mine wastes with uniform (flat) or complex (sloping) surfaces. Those that are constructed on relatively flat surfaces (e.g., tailings) are referred to as layered CCBEs (Figure 1.1 (a)), whereas inclined CCBEs (Figure 1.1 (b)) are those which are used on complex surfaces (e.g., waste rock piles, large dykes) (Aubertin et al., 2009). Inclined CCBEs limit the occurrence of local desaturation in the moisture retaining layers on sloping mine wastes, unlike layered CCBEs (Aubertin et al., 2009). Previous on-site studies, such as those carried out at the Equity Silver Mine (O'kane et al., 1998; Weeks & Wilson, 2005), the Manitou site (Bussière et al., 2007; Molson et al., 2008), and the Lorraine site (Dagenais et al., 2005) confirmed the efficacy of CCBEs in limiting O₂ ingress and subsequent AMD generation. The

materials required for the construction of CCBEs, however, may be costly, difficult to install or not available in adequate quantities (Kalonji et al., 2017).

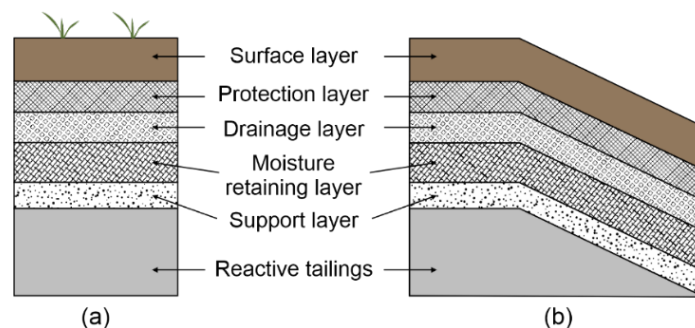


Figure 1.1. Typical configurations of capillary barrier effects (CCBEs) used to limit O_2 influx to the reactive tailings: (a) layered CCBEs are usually applied on relative flat surfaces (e.g., mine tailings), (b) inclined CCBEs are usually applied on complex surfaces (e.g., waste rock piles, large dykes) to limit local desaturation in the moisture retaining layer (adapted from Aubertin et al., 1995).

1.1.4.3 Barrier-type Cover Systems

Barrier-type cover systems incorporate one or more materials with low O_2 diffusivities to minimize sulfide-mineral oxidation. Synthetic soil liners, permafrost aggradation covers, and geomembranes are the most commonly used barrier-type cover systems. The application of synthetic soil liners involve the use of one or more soil layers. The layer(s) could be compacted locally available silt/clay, concrete-type layer, or sand-bentonite (MEND, 2012). In Bersbo (Sweden), for instance, barrier-type cover systems that included a 0.5 m layer of compacted glacial clay and a 0.25 m layer of concrete-type layer referred to as Cefyll (made from a mixture of cement and fly ash) were used to cover the Steffenburg dump and the Storgruve dump, respectively (Figure 1.2). The measured concentrations of O_2 underneath the covers were insignificant, confirming their effectiveness (Lundgren, 2001). These covers, however, are expensive to design and may be susceptible to freeze-thaw cycles and root penetrations (Lundgren, 2001). The soil liners constructed of bentonite (e.g., sand-bentonite) are also susceptible to cation exchange reactions; for instance, exchanging monovalent sodium ions in bentonite for divalent ions in the surrounding soil will reduce bentonite swelling

and increase hydraulic conductivity (Buckley et al., 2012; Bradshaw et al., 2013), which in turn can allow O_2 to ingress. Furthermore, interaction of bentonite with acidic solutions can increase porosity and reduce swelling, allowing O_2 to ingress due to increased hydraulic conductivity (Fall et al., 2009; Shackelford et al., 2010). Covers with low permeable material(s) are also susceptible to erosion due to reduced infiltration (MEND 2012).

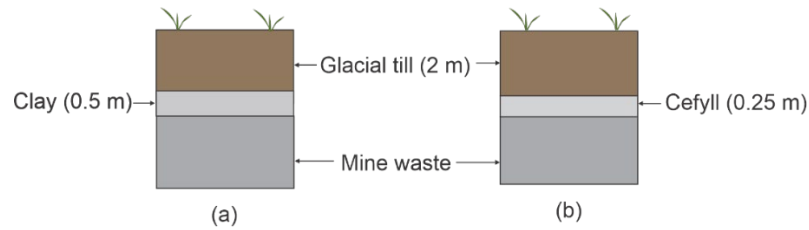


Figure 1.2. Composition of cover materials placed over the Bersbo waste rock piles. The cover systems in (a) and (b) were constructed over the Steffenburg dump and the Storgruve dump, respectively. Cefyll (trade name) is a concrete-type material made from a mixture of cement and fly ash to enhance stability. Cefyll was grouted into 0.25 m of crushed rocks to minimize sulfide-mineral oxidation.

1.1.4.4 Permafrost Aggradation Covers

Permafrost aggradation covers are restricted to permafrost regions. In these regions, AMD generation can be limited by freezing and keeping the reactive wastes in a frozen state to reduce the influx of O_2 (due to low diffusion capacity of a frozen material) and to retard microbial activities (due to very low temperatures in these regions). For example, a permafrost aggradation cover composed of a 1.0 m granular shale fill and a 0.25 m surface armour (composed of gravels and cobbles) was installed over the Nanisivik Mine, Nunavut, Canada (Cassie, 2015) (Figure 1.3). The results of the long-term monitoring program showed that stable conditions were achieved, indicating that this reclamation approach is effective in minimizing the generation of AMD. Permafrost aggradation covers, however, are costly to design, susceptible to global warming, and may take time to develop (MEND 2012).

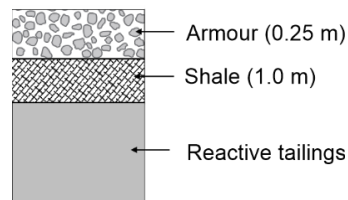


Figure 1.3. Composition of cover materials placed over the Nanisivik Mine tailings. The armour layer is composed of gravels and cobbles.

1.1.4.5 Bactericides

Bactericides, mainly anionic surfactants, are usually introduced directly to mine wastes or blended with them to inhibit bacteria and therefore limit the rate of sulfide-mineral oxidation. Stichbury et al. (1995), for example, proposed the use of thiol-blocking compounds to inhibit the bacteria that participated in the early stages of sulfide oxidation. Over a one-year period, Stichbury et al. (1995) reported reduced sulfide-mineral oxidation in column studies. During a two-year field study, the inhibitor mixture reduced the development of *Thiobacillus thioparus* and *At. thiooxidans* and totally inhibited the growth of *At. ferrooxidans* (Lortie et al., 1999). Concentrations of SO₄, Fe, and other dissolved elements were lower in treated plots than in untreated control plots. The inhibitors were observed to lose effectiveness within the initial year post-application, indicating that they are not suitable for prolonged use. This observation indicates that inhibitors might be most beneficial when used in situations where prevention of sulfide-mineral oxidation is necessary for only short periods of time.

1.1.4.6 Geomembranes

Geomembranes are synthetic membrane liners that are made from continuous polymeric sheets that can be thermally or chemically melted together at the seams for strength, size, and durability, and placed on mine wastes (Figure 1.4). In Poirier Mine tailings (Joutel, Québec), for instance, a high-density polyethylene membrane was constructed over the tailings with a protective earthen cover over the membrane. The results of the long-term evaluation showed insignificant sulfide-mineral oxidation, confirming its efficacy (Hogan & Tremblay, 2010).

The use of geomembranes, however, has several drawbacks. According to MEND (2012), most geomembranes are subject to sunlight degradation, physical penetration (e.g., root penetration) and need to be protected by covering with an earthen cover. The impermeable nature of geomembranes, however, may cause solifluction in earthen covers on sloping surfaces.

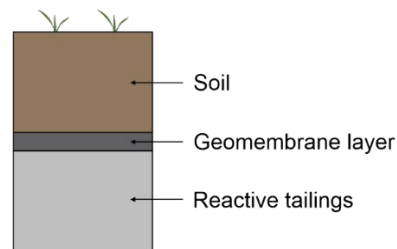


Figure 1.4. Schematic diagram of a barrier-type cover system using a geomembrane liner to limit O₂ ingress (adapted from MEND, 2012).

1.1.4.7 Organic Covers

In addition to covers that limit O₂ ingress, covers that consume O₂ have been applied to the surface of mine tailings (Tassé et al., 1994; Peppas et al., 2000). These cover systems, commonly referred to as organic covers, generally involve the emplacement of covers containing organic matter, mainly lignocellulosics (e.g., sawdust, wood chips, wood waste, sewage sludge) (MEND, 1994). The goal is to consume O₂ by reacting with the organic matter, thereby limiting O₂ interaction with the underlying sulfide minerals, potentially minimizing the generation of low-quality drainage and release of toxic elements. This reaction is expressed by Peppas et al. (2000) as:



where C₆H₁₂O₆ represents a generic organic compound. The application of organic covers, however, has some limitations. According to Ribet et al. (1995), organic covers may promote microbially mediated reductive dissolution of Fe(III) (oxy)hydroxide phases, resulting in the release of Fe(II) and other metal(loid)s previously coprecipitated with, or adsorbed onto them, to the environment. Additionally, the mass of the organic matter required to prevent sulfide-mineral oxidation in the long term may be unsustainable since it needs to be constantly replenished (Reardon & Poscente, 1984; Hulshof et al., 2003).

1.1.4.8 Covers Utilizing Elevated Water Table (EWT) Technique

The EWT technique is a promising and lower cost alternative for the long-term control of sulfide-mineral oxidation and subsequent acid mine drainage generation (MEND, 1996), from an abandoned tailings impoundment such as the one represented by a generic diagram in Figure 1.5. The key design approach is to elevate the water table above the reactive tailings to restrict the interaction of O_2 with reactive tailings. This can be achieved by adding a layer of inert, coarse-textured material (e.g., gravel) or fine-textured material (e.g., desulfurized tailings), as a cover, and maintain the water table within this layer (Dagenais et al., 2006; Ouangrawa et al., 2009; Maqsoud et al., 2019). The use of a coarse-textured layer coupled with the EWT technique can increase percolation and minimize water loss by evaporation (Dagenais et al., 2006; Ouangrawa et al., 2009), therefore improving water balance, whereas a fine-textured layer can promote water retention and prevent the diffusion of O_2 (Mbonimpa et al., 2003; Dobchuk et al., 2013). Studies (Dagenais et al., 2006; Ouangrawa et al., 2009) have shown that the EWT technique is very efficient in restricting sulfide-mineral oxidation and AMD generation from unoxidized tailings.

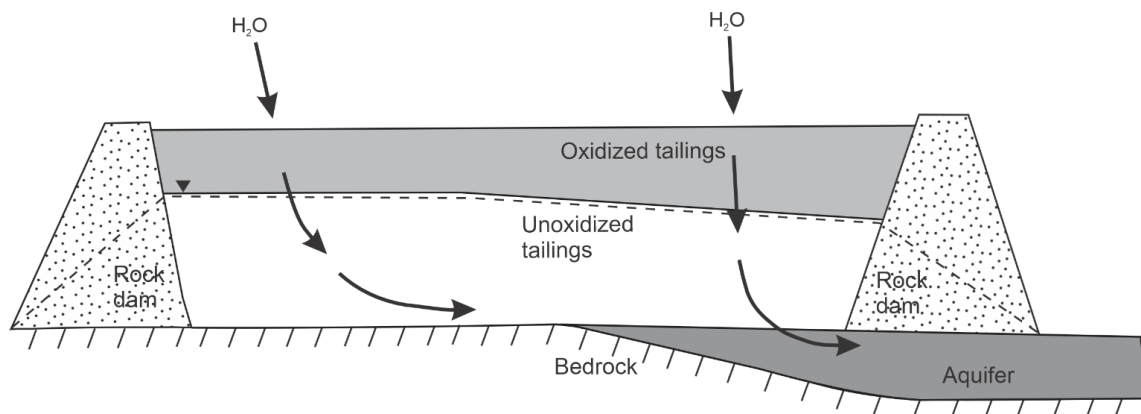
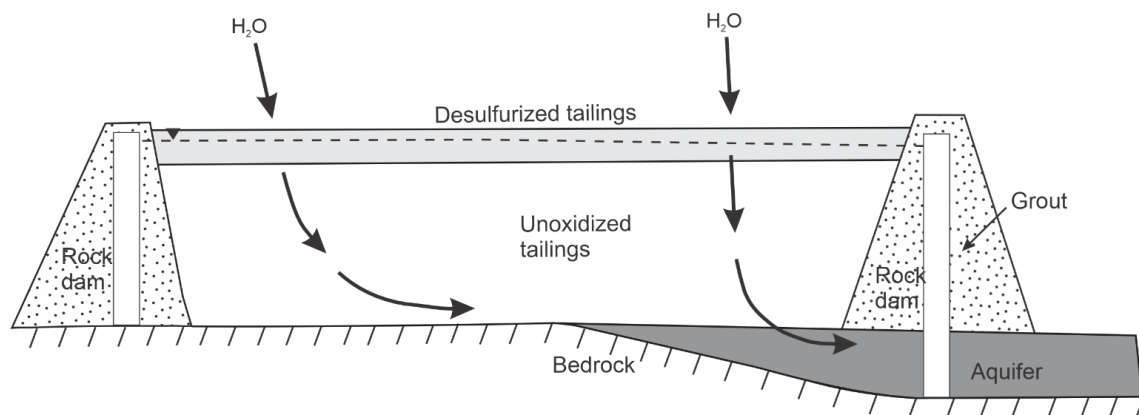
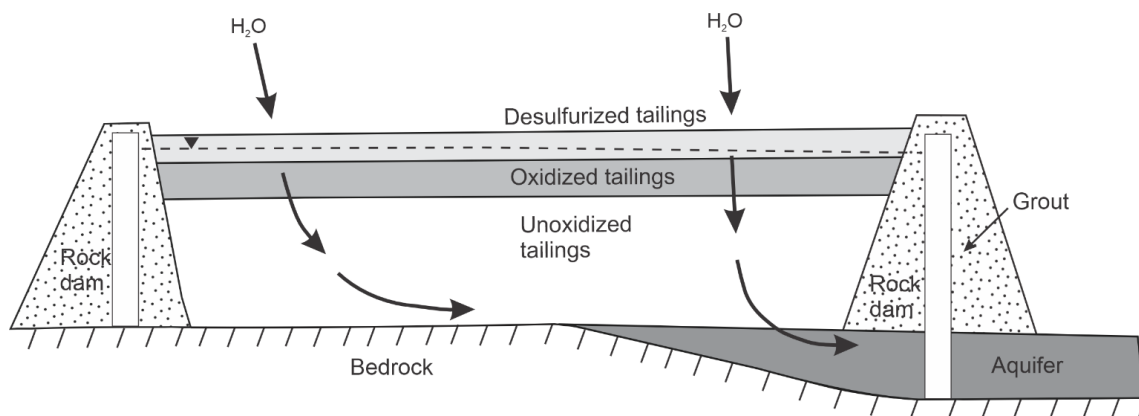


Figure 1.5. Schematic diagram of an uncovered tailings.

As with all the tailings cover systems, the EWT technique is highly effective when it is applied immediately after tailings disposal ceases (Gunsinger et al., 2006; Blowes et al., 2014), as illustrated in Figure 1.6 (a). A delayed application of the EWT technique, however, is not beneficial since sulfide-mineral oxidation and metal(loid)s release are highest in the first few years to decades after tailings disposal is completed because the moisture content increases with depth, slowing down the oxidation rates (Gunsinger et al., 2006; Blowes et al., 2014). Furthermore, the use of cover systems that involve the submergence of oxidized tailings, such as the EWT technique, usually causes the dissolution of soluble secondary phases (e.g., gypsum) as well as the potential inducement of reducing conditions that are ideal for microbially mediated reductive dissolution of secondary Fe(III) phases and concomitant release of associated toxic metal(oids) to the environment (Figure 1.6 (b)).



(a)



(b)

Figure 1.6. Schematic diagrams of two configurations of the EWT system. The EWT system in (a) shows desulfurized tailings overlying unoxidized tailings and (b) shows desulfurized tailings overlying partially oxidized tailings.

1.1.5 Mineralogical Study and Chemical Extractions

Mineralogical analysis allows the determination of various mineral phases as well as the locations of associated metal(loid)s in the tailings. Mineralogical analysis, however, is not well suited to characterizing the concentrations of metal(loid)s since it requires a comprehensive microscopic analysis of a representative number of mineral grains (Ribet et al., 1995). Alternatively, chemical extractions, which involve the use of reagents to dissolve specific fractions of tailings samples based on their chemical properties, are often used to achieve the same objectives. Ribet et al. (1995), for example, used a mineralogical analysis coupled with a two-phase chemical extraction procedure to characterize metal(loid)s associated with a reducible fraction in a carbonate-depleted Nickel Rim mine tailings, Sudbury, Canada; however, since some constituents can potentially be associated with carbonate minerals, chemical extraction methods on mine tailings samples that contain significant quantity of carbonate minerals will differ. Gunsinger et al. (2006), for instance, used a five-phase extraction procedure to target five different fractions in mine tailings that contained some carbonate minerals.

While chemical extractions are widely used to determine the distribution of metal(loid)s in mine tailings, there are still some significant limitations. One key limitation is that the chemical extraction results are operationally defined and do not reflect actual solid-phase speciations and cannot be verified (Tessier et al., 1979; Nirel & Morel, 1990). Additionally, the chemical conditions used during extraction procedures cannot be extended to simulate natural conditions due to differences in chemical compositions and kinetic rates (Nirel & Morel, 1990).

1.1.6 Mining in Chibougamau

Mining in Chibougamau is associated with a layered stratiform intrusion known as the Lac Doré Intrusive suite that is divided into four zones: the anorthositic zone, the layered zone, the granophyre zone, and the border zone (Golder Associates, 2011). The anorthositic zone is the thickest and the most important zone of the suite, with a thickness of up to 3 km and serving as the host rock for the majority of Chibougamau's copper-gold deposits. The rock composition of the anorthositic zone ranges from meta-gabbro to meta-anorthosite and are Archean in age. Toward the south-eastern part of the site is the Chibougamau Pluton, which is an igneous intrusion composed of dioritic-tonalitic rocks that cut across the anorthositic zone of the suite, creating a km-wide gap. According to Larouche (2012), the contact is associated with many of the ore deposits that generally occur as sulfide veins and porphyry-style deposits that contain sulfide minerals (10 - 30%) comprised mainly of pyrite, chalcopyrite with some pyrrhotite (1 - 5%) along with minor amounts of sphalerite and galena. The ore matrix consists of chlorite (70 - 90%) with small amounts of quartz and carbonate minerals estimated between 15% to 20%. Mining of the deposits started in the 1950s and about 1.6 billion pounds of copper and 3.2 million ounces of gold were produced along with significant amounts of silver and zinc, producing approximately 26 million tonnes of ore (1.6 wt.% Cu and 0.3 g Au/t) from at least 12 separate deposits in the region (Maqsoud et al., 2019). Tailings from ores processing were stored in three tailings storage facilities at Mine Principale designated as Parc A, Parc B, and Parc C. Mine Principale is located near the town of Chibougamau, Quebec. The focus of this study was Parc B. Parc B covers an approximate area of 560,000 m², and it was filled up to depths of up to 13 m with sulfidic tailings.

1.2 Research Objectives

The research studies present a multi-disciplinary approach to determining the potential impacts of using the EWT approach on partially oxidized tailings of Mine Principale. The studies focus on the following research questions: i) What secondary phases present in the oxidized zone that may be affected by direct and reductive dissolution reactions? ii) What are the concentrations of metal(loid)s associated with these secondary phases? iii) Are iron- and sulfate-reducing bacteria present in the oxidized tailings? iv) What is the organic matter content of the oxidized tailings?

1.3 Organization of Thesis

The contents of this thesis will be divided into three chapters. The first chapter presents a global overview of mine wastes, geochemical processes, and common sulfide-mineral oxidation controls. The second chapter presents the characterization of secondary phases that are susceptible to direct and reductive dissolution reactions, as well as the associated metal(loid)s. Results of microbiological DNA extraction and analysis are also presented in chapter two. Finally, chapter three presents the overall summary and conclusion.

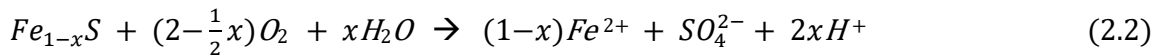
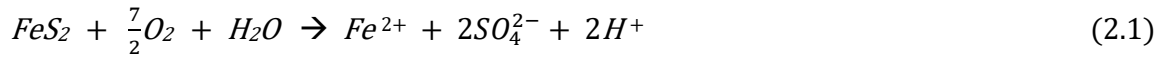
Chapter 2: Geochemical Characterization of Parc B Tailings

2.1 Summary

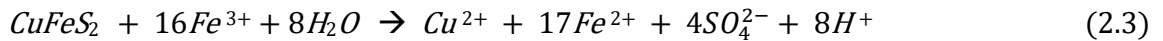
Oxidation of sulfide minerals in Mine Principale tailings has resulted in the generation of low-quality pore-water laden with elevated concentrations of Fe, SO₄, and other dissolved hazardous metal(loid)s including Cu, Co, Ni, and Zn. This study focused on the tailings stored in Parc B that are about 10 m deep. Parc B was constructed in 1962, covering approximately 56 hectares of land, and remained operational until the late 1980s or early 1990s. During that time, tailings from approximately nine separate mines in the region were deposited, significantly contributing to the geochemical complexity of the site. Tailings deposited in Parc B have undergone oxidation for more than 50 years, resulting in the advancement of low-pH pore-water and elevated concentrations of hazardous metal(loid)s at depths. High concentrations of dissolved hazardous metal(loid)s (up to 1800 mg L⁻¹ Fe, 100 mg L⁻¹ Cu, 40 mg L⁻¹ Co, 20 mg L⁻¹ Ni, and 7 mg L⁻¹ Zn) were observed in the tailings pore-water. Oxidation of predominant sulfide minerals, pyrite and pyrrhotite, has led to the depletion of hazardous metal(loid)s in the shallow tailings. Results from amplicon sequencing of 16S rRNA genes reveal significant presence of sulfur- and/or iron-metabolizing bacteria in the tailings. Solid-phase analyses indicate a low amount of total carbon in the oxidized tailings; however, given the presence of vegetation at the site, the organic carbon content may increase over time. Results of non-sequential chemical extractions indicate that significant concentrations of these hazardous metal(loid)s are associated with Fe(III) (oxy)hydroxide phases. Application of the proposed EWT technique could thus create reducing conditions that are ideal for microbially catalyzed reductive dissolution of Fe(III) (oxy)hydroxide phases and attendant release of associated hazardous metal(loid)s to the environment if labile organic C increases in the tailings impoundment.

2.2 Introduction

Sulfide-mineral oxidation generates acid mine drainage (AMD) characterized by high concentrations of Fe, SO₄, and other dissolved metal(loid)s. Elevated concentrations of dissolved Fe, Cu, Co, Zn, and Ni observed in the tailings water were expected based on the known sulfide-ore assemblage reported in previous studies conducted on the site (Golder Associates, 2011; Larouche, 2012). Shallow tailings of Mine Principale are ochreous in color as a result of decades of exposure of sulfide minerals to atmospheric conditions. Pyrrhotite [Fe_(1-x)S] and pyrite [FeS₂] are the principle sulfide minerals at the site (Golder Associates, 2011). A significant quantity of chalcopyrite [CuFeS₂] as well as minor quantities of sphalerite [(Zn,Fe)S], pentlandite [(Fe,Ni)₉S₈], arsenopyrite [FeAsS], and galena [PbS] are also present in the tailings (Larouche, 2012) and can release hazardous metal(loid)s such as Cu, Ni, Co, Zn, As, and Pb, upon oxidation. Dissolution of silicate minerals can result in the release of metals including Al, Mn, and Cr into the pore-water. The oxidation of principal sulfide minerals, pyrrhotite and pyrite, are the primary cause of elevated concentrations of Fe and SO₄ in the pore-water and are described in reactions (2.1) and (2.2), respectively:

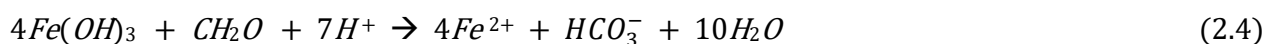


The release of Cu and Fe, as well as the consumption of H⁺, result from the oxidation of chalcopyrite by O₂. However, further oxidation of Fe(II) and S⁰ can generate H⁺:



Oxidation of sulfide minerals can also be facilitated by bacteria. Sulfide minerals that dissolve in acid (e.g., sphalerite) can be oxidized by acidophilic bacteria such as *Acidithiobacillus thiooxidans*, resulting in the generation of sulfuric acid. Acid-insoluble sulfide minerals (e.g., pyrite) can be indirectly oxidized by bacteria like *Leptospirillum* spp. which oxidize ferrous iron to ferric iron. Ferric iron is the most significant oxidizing agent for sulfide minerals compared to molecular oxygen in acidic solutions (Blowes et al., 2014).

Oxidation of sulfide minerals can also result in the formation of secondary Fe(III) (oxy)hydroxide and (oxy)hydrosulfate phases, such as goethite [α -FeOOH], ferrihydrite [$\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$], and jarosite [$\text{KFe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2$]. Extensive precipitation of these minerals together with other cementing minerals such as gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$] can result in the formation of hardpan layers commonly observed in many abandoned mines (Moncur et al., 2005; Gunsinger et al., 2006; DeSisto et al., 2011; Elghali et al., 2019). Hardpan layers are linked to the attenuation of SO_4 via the precipitation of gypsum and also can act as a barrier to the progress of sulfide-mineral oxidation by limiting the downward migration of low-quality pore-water and O_2 . Iron(III) (oxy)hydroxide and (oxy)hydrosulfate phases can also incorporate hazardous metal(loid)s into their structures through co-precipitation or adsorption reactions, which can be released to groundwater through microbially catalyzed reductive dissolution reactions:



Sulfide-mineral oxidation can be minimized by limiting the amount of oxygen interacting with sulfidic wastes and restricting the growth of oxidizing microorganisms in abandoned mine sites. The commonly used $\text{O}_{2(\text{g})}$ transport barriers are water covers (Awoh et al., 2013; Moncur et al., 2015), which restrict O_2 transport due to its low diffusion coefficient in a layer of water (Mbonimpa et al., 2003; Adu-Wusu & Yanful, 2006), covers with capillary barrier effect composed of materials that maintain high degrees of saturation and low gas-phase diffusivities (Bussière et al., 2003; Dagenais et al., 2005; Kalonji et al., 2017), barrier-type covers made of materials with low O_2 diffusivities (Lundgren, 2001), covers composed of oxygen-consuming materials (Tassé et al., 1994; Peppas et al., 2000), and covers designed to promote an elevated water table that also take advantage of the low diffusion coefficient of O_2 in saturated or nearly saturated porous media (Dagenais et al., 2006; Ouangrawa et al., 2010; Maqsoud et al., 2019). Bacterial activity is inhibited by the application of bactericides, most notably anionic surfactants (Blowes et al., 2014).

Since Mine Principale tailings have been identified as having acid generating potential, the reclamation of the site is necessary in order to limit the generation of AMD (Maqsoud et al., 2019). The reclamation strategy proposed is a cover utilizing the elevated water table (EWT). The concept behind the

EWT technique is to raise and maintain the water table in a position that maintains the reactive tailings at a sufficiently high degree of water saturation. This high degree of saturation minimizes tailings oxidation. Studies have shown that the EWT technique is very effective in restricting sulfide-mineral oxidation when it is applied on unoxidized tailings (Dagenais et al., 2006; Ouangrawa et al., 2009). The use of the EWT technique, however, involves the submergence of oxidized tailings, which can result in the dissolution of soluble secondary phases (e.g., gypsum). The EWT technique can also induce reducing conditions that are ideal for microbially catalyzed reductive dissolution of Fe(III) (oxy)hydroxide and (oxy)hydrosulfate phases and concomitant release of associated hazardous metal(loid)s to the environment in the presence of labile organic C. The main objective of this study is to evaluate the potential impacts of applying the EWT technique on partially oxidized tailings of Mine Principale. Assessing the potential impacts will help determine whether or not this proposed reclamation technique will be effective.

2.3 Site Description

Mine Principale is an abandoned copper-gold mine site located on Merrill Island in Lac aux Dorés about 5 km southeast of the city of Chibougamau, Québec, Canada (Figure 2.1). It is located in a subarctic region characterized by long, cold, and snowy winters, and warm but shorter summers. The average annual precipitation is about 4126 mm, with snow making up about 75.8% of the total precipitation. Significant precipitation occurs throughout the year except in the months of February, March, and April when drier conditions prevail (Environment Canada, 2003).

Mine Principale was operational from 1955 to 1980 under the ownership of Campbell Resources. It continued to be used as a milling and storage facility for tailings from at least 12 separate deposits in the region until its closure in 2004. Tailings produced during the mining activities, estimated to be between 18.8–19.2 million tonnes, were deposited in three separate tailings impoundments designated as Parc A, Parc B, and Parc C, at different times between 1955-2004 (Table 2.1). The tailings in these impoundments cover

approximately 170 hectares of land (Golder Associates, 2011). After mining ceased, Campbell Resources went bankrupt, prompting the Ministry of Natural Resources to take control in 2010 (Maqsoud et al., 2019).

Table 2.1. Potential deposition sites for different mine tailings based on mine production and tailings impoundments timelines (Larouche, 2012).

Mine	Production	Minerals	Metals	Potential Parc
Mine Principale	1955 - 1980	Feldspar, sphalerite, pyrite, chalcopyrite, quartz, chlorite, sericite, carbonate	Au, Cu, Ag	A/B/C
Cedar Bay	1958 - 1990	Arsenopyrite, chalcopyrite, pyrite, sphalerite, pyrrhotite, chlorite, sericite, carbonate	Au, Cu, Ag, Zn, Co, As	A/B/C
Merril	1959 - 1968 & 1971 - 1980s	Chlorite, sericite, quartz, chalcopyrite, pyrrhotite, pyrite, sericite, chlorite, carbonate	Au, Cu, Ag	A/B/C
Kokko Creek	1960 - 1964	Chalcopyrite, gold, silver, pyrite, pyrrhotite, sphalerite	Cu, Au	A/B
Henderson I	1960 - 1971	Pyrite, pyrrhotite, quartz, chalcopyrite, carbonate, sericite	Cu, Au	A/B/C
Henderson II	1960 - 1988	Sphalerite, arsenopyrite, pyrite, pentlandite, chalcopyrite, pyrrhotite, carbonate, chlorite, sericite	Cu, Au, Ag, As, Ni	A/B/C
Chib-Kayrand	1964 - 1974	Quartz, chalcopyrite, pyrite, sphalerite, galena, pyrrhotite, chlorite, sericite, carbonate	Cu, Ag, Pb, Zn, Mo, Au	A/B/C
Grandroy	1967 - 1969	Chalcopyrite, gold, molybdenite, pyrite, magnetite, hematite, carbonate	Cu, Au, Mo	B
Obalski	1983 - unknown	Pyrite, chalcopyrite, sphalerite, pyrrhotite, quartz, carbonate	Cu, Au, Ag, Zn	C
Joe Mann	1987 - 2004	Quartz, carbonate, pyrite, chalcopyrite, pyrrhotite, arsenite	Cu, Au, Ag, As	C
S-3	1987 - 1990	Chalcopyrite, sphalerite, quartz, chlorite, carbonate, sericite	Cu, Au, Ag	C
Gwillim Lake	1979 - unknown	Carbonate, quartz, chlorite, pyrite, chalcopyrite,	Au, Cu, Ag	C
Devlin	1982 - unknown	Magnetite, chalcopyrite, pyrite, chlorite, sericite	Cu, Au, Ag, Mo, W, Bi, As, Co, Sb	C
Copper Rand	1960 - 2004	Magnetite, chalcocite, malachite, chalcopyrite, pyrite, pyrrhotite, chlorite, carbonate, silica	Cu, Au, Ag	A/B/C

Parc A was built in 1955 and tailings from at least eight separate deposits were stored there from 1955 to the 1960s, reach depths of up to about 10 m. Surface samples collected from the southern part of Parc A in 2002 consisted of 46.6% quartz, 36.7% ankerite, 6.1% calcite, and 2.1% pyrite (Golder Associates, 2011). Parc A tailings have been identified as having the potential to generate AMD (Maqsoud et al., 2019). Restoration work that included covering the surface of the tailings with wood ash and tailings pumped directly from the mill plants, as well as revegetation program, was carried out from 1989 to the 1990s, but the effectiveness of this work has not been documented.

Parc B was built in 1962 and was operational until the late 1980s or early 1990s. During that period, tailings from at least nine separate mines were also stored in Parc B. A revegetation programme was attempted in Parc B in 1992 and 1993, however due to the acidity of the surficial tailings, it proved unsuccessful. Surface samples collected in 1999 and 2001 indicated the presence of chlorite (27 - 35%), plagioclase (30 - 38%), quartz (7 - 17%), and small amounts of calcite. Tailings contained within this storage facility reach depths of up to about 10 m and have the potential to generate AMD as well.

Parc C was built in the early 1970s and contains tailings associated with numerous separate mines. Tailings stored in Parc C reach depths up to about 14 m, and the sulfur-sulfide content of the samples ranges from 0.84 – 0.94%. Tailings from Parc C have the low potential to generate AMD and as a result, they are being considered for use as a cover layer for the EWT (Maqsoud et al., 2019).

Groundwater flows from Mine Principle to Lac aux Dorés in all directions, but with varying velocities. The velocities of groundwater flow from Parcs A, B, and C to Lac aux Dorés are 1000 m³/year, 8.5 m³/year and 2 m³/year, respectively (Golder Associates, 2011).

The study focused on tailings samples collected in November 2020 from Parc B. Samples were collected from Mpr20-4, Mpr20-5, and Mpr20-6 as shown in Figure 2.2. The sulfide content of Parc B tailings in these 3 locations range from 3.4 wt% in areas distal to the point of tailings discharge (e.g., Mpr20-4) to approximately 10.6 wt% in the zones proximal to the point of tailings discharge (e.g., Mpr20-5

& Mpr20-6). This study focuses on tailings from Mpr20-4 and Mpr20-6 since the extent of oxidation is similar between Mpr20-5 and Mpr20-6 but different from Mpr20-4.

The reclamation plan proposed to minimize further sulfide-mineral oxidation in the Mine Principale tailings is the EWT technique (Maqsoud et al., 2019), which will potentially involve the use of fine-grained desulfurized tailings from Parc C as a cover material. Because the tailings at the site have been long exposed to O₂ and are visibly oxidized as a result, application of the EWT technique is expected to result in the remobilization of metal(loid)s previously sequestered in various secondary phases, particularly Fe(III) (oxy)hydroxides.

The main goal of the Mine Principale project is to characterize hazardous metal(loid)s that can be released from secondary phases under the EWT scenario. Characterization of secondary phases and determination of the localities of associated metal(loid)s were achieved using various mineralogical investigations including optical microscopy, scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), X-ray powder diffraction (XRD), X-ray fluorescence spectroscopy (XRF), and micro-X-ray fluorescence spectroscopy (μ -XRF). Non-sequential chemical extractions were performed to determine the concentrations of metal(loid)s associated with various secondary phases, and microbiological deoxyribonucleic acid (DNA) extraction was performed to determine the availability of microbiological species that may fuel reductive dissolution reactions. The organic matter present in the tailings was estimated using solid-phase analyses. All these analyses were performed on sample cores collected from Parc B in November 2020. Parcs A and C were not studied since Starzynski (2020) had already completed a similar study using sampled cores from Parc A, and no sampled cores from Parc C were collected for analysis because of time constraint due to COVID-19 restrictions at the time.

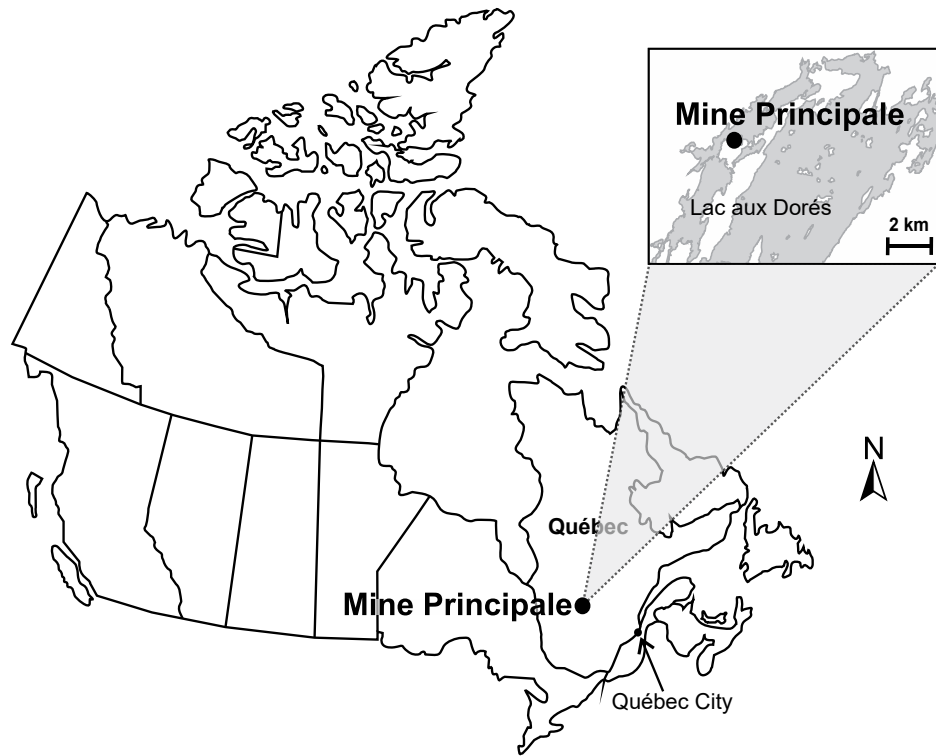


Figure 2.1. Location of Mine Principale, Québec, Canada.

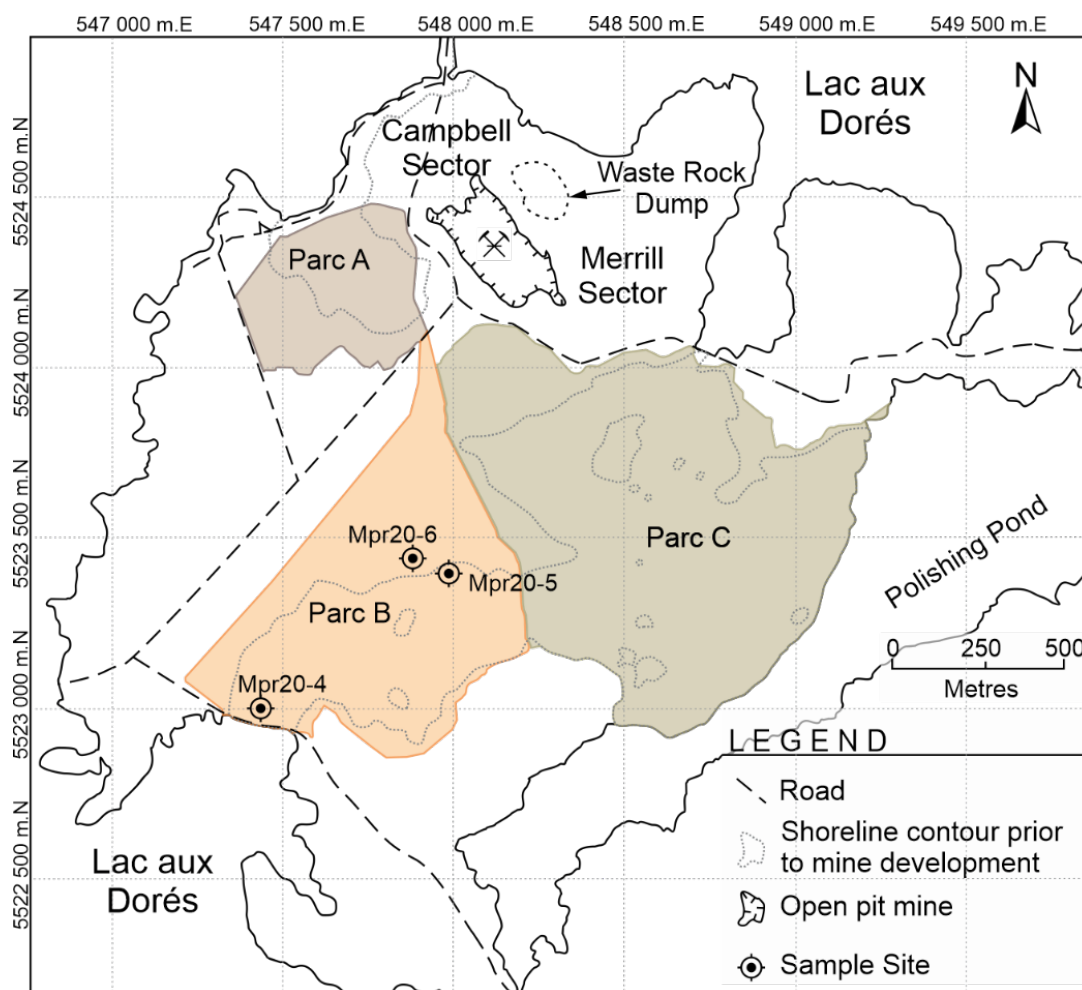


Figure 2.2. Sampling locations in Parc B.

2.4 Materials and Methods

2.4.1 Geochemical Sampling

In November 2020, three continuous cores extending from the tailings surface to a depth of about 2-3 meters below ground surface (mbgs) were collected in thin-wall Al tubes of 5.1 or 7.6 cm diameter from each location in Parc B of Mine Principale and immediately capped and sealed with low-density polyethylene to minimize exposure to atmospheric oxygen. Upon arrival at the University of Waterloo, cores were immediately placed upright in the cold room at 4°C, and immediately cut into about 40 cm sections, sealed, and stored in a freezer at -18°C. Measurements of O₂ and CO₂ in the field were made with Quantek portable meter and steel drive-point gas rods at 10 cm increments from the surface of the tailings to the depth of O₂ depletion in two sampling locations because the third location was extremely wet. The volumetric water content and temperature were measured in 10 cm increments in a hand shovelled pit adjacent to the location of gas measurements, using Decagon 5TM probes and an FM50 datalogger, respectively. The tailings near the surface have been exposed to atmospheric oxygen for years at the time of sampling, and the surficial tailings are visibly oxidized.

2.4.2 Pore-water Analysis

The squeezing technique described by (Moncur et al., 2013) was used to extract pore-water from sample cores that were cut into about 25 cm core sections and collected in 60-mL polyethylene syringes. All pore-water samples in 60-mL PE syringes were filtered through 0.45 µm cellulose-nitrate filters and then transferred to pre-washed two polyethylene bottles. One aliquot was preserved at a pH < 2 with Omni Trace metal grade nitric acid (HNO₃) for major cation and minor and trace element analyses. The other aliquot was left unacidified for the analysis of anions. All pore-water samples were immediately refrigerated at 4°C until analysis. Analyses for major and minor cations, trace elements, and anions were conducted using ICP-OES, ICP-MS, and IC, respectively. Measurements of pH, Eh, and alkalinity were made immediately after pore-water extractions in the laboratory. Measurements of pH and Eh were made on unfiltered samples at least three times to obtain representative results. The pH was measured using a pH electrode (Orion

8156BNUWP, Thermo Scientific, USA) that was calibrated with standard buffer solutions at pH 4, 7, and 10.0. The Eh was measured using an Eh electrode (Orion 9678BNWP, Thermo Scientific, USA), which was checked against Zobell's solution (Nordstrom, 1977) and Light's solution (Light, 1972). Measurement of alkalinity was made on filtered samples by titrating with a Hach digital titrator containing 0.16 N H₂SO₄ to the bromcresol green-methyl red indicator.

2.4.3 Geochemical Modelling

The aqueous geochemical measurements were used to simulate geochemical speciation and the degree of saturation with respect to various minerals, represented as the saturation index (SI). The geochemical speciation and SI were interpreted with assistance of the equilibrium/mass-transfer model PHREEQC (Parkhurst & Appelo, 2013) using the WATEQ4F geochemical database (Ball & Nordstrom, 1991) for each sample location. PHREEQC uses geochemical parameters such as pH, pe, temperature as well as element concentrations in solution to determine the distribution of redox species and saturation indices, helping predict phases that are thermodynamically favourable. Equilibrium is indicated by a SI value of zero, while undersaturation is indicated by a negative value and supersaturation is indicated by a positive value.

2.4.4 Tailings Solids

Core samples of the tailings solids were collected in November 2020 for solid-phase analyses. One continuous core from each location was sectioned along its length and samples were collected and used for mineralogical study, non-sequential chemical extraction, microbiological study, X-ray fluorescence (XRF) analysis, X-ray absorption spectroscopy (XAS), measurements of total carbon and sulfur content, bulk density, and gravimetric moisture content, based on visual changes. Physical properties of the tailings were determined through measurements of grain-size distribution, bulk density, and particle density. Grain size analysis was conducted using a laser particle sizer (ANALYSETTE 22 NeXT Micro). The particle density was measured with an air comparison pycnometer (Beckman model 930). Bulk density and moisture content were measured gravimetrically using samples of known volumes after oven-drying them at approximately

80°C for 24 hours. The porosity and volumetric moisture content were calculated from the measured bulk density, gravimetric moisture content, and particle density.

Sub-samples for mineralogy, selective chemical extractions and microbiological study were collected in the COY anaerobic chamber. Selective chemical extractions were done immediately following the sampling events in the laboratory. Sub-samples for mineralogy and microbiological study were immediately stored in a regular freezer (at -18°C), and a deep freezer (at -80°C), respectively, until analysis. Sub-samples for polished thin sections were freeze-dried and sent to Vancouver Petrographics Ltd, where they were prepared with non-aqueous epoxy, double polished to 60 µm thickness, and mounted on glass slides. The polished thin sections were examined using reflected and transmitted light microscopy (Nikon Eclipse LV100N-POL) and with scanning electron microscopy with energy dispersive spectrometry (SEM-EDS; Hitachi TM3000, QUANTAX 70 EDS) at the University of Waterloo. Sub-samples for µ-XRD and XRF were dried in the open inside the COY anaerobic chamber and pulverized with the Wig-I-Bug before being analyzed for powder XRD and XRF at the Canadian Light Source synchrotron facility in Saskatoon and the University of Waterloo, respectively. Qualitative observations of sulfide alteration in tailings depth profile were made based on sulfide alteration index (SAI), which is a numerical scale that was developed by Jambor (1994) (Table 2.2). The extraction of microbiological DNA was carried out according to the instructions outlined in the Qiagen DNeasy PowerSoil Pro Kit.

Table 2.2. Sulfide Alteration Index (SAI) of tailings from site Mpr20-6.

Index	Degree of alteration
10	Almost complete depletion of sulfides; traces of chalcopyrite and pyrite present
9	Only scarce pyrite and chalcopyrite; no pyrrhotite or sphalerite
8	Pyrite and chalcopyrite common; traces of pyrrhotite and sphalerite present
3-7	At index 7 pyrrhotite grains have broader alteration rims with cores preserved in numerous grains. At index 3, alteration rims are narrower
2	Well-developed cores of pyrrhotite with narrower alteration rims
1 - 0	Alteration is restricted to narrow rims on < 5% of pyrrhotite grains

Table 2.3. Sulfide Alteration Index (SAI) of tailings from site Mpr20-4.

Index	Degree of alteration
3	Pyrrhotite grains have alteration rims that are narrow
2	Well-developed cores of pyrrhotite with narrow alteration rims
1 - 0	Alteration is restricted to narrow rims on few pyrrhotite grains

2.4.5 Carbon and Sulfur Analysis

Carbon and sulfur contents were measured using an ELTRA CS 2000 induction and resistance furnace.

Samples were dried in the open inside the COY anaerobic chamber before being combusted at 1350⁰C, and the release CO₂ and SO₂ were measured by infrared detection.

2.4.6 X-ray fluorescence (XRF) Analysis

Samples for XRF analysis were dried inside the COY anaerobic chamber before being pulverized and analyzed in the laboratory using XRF (PANalytical MiniPal 4) to determine trace elements and major rock-forming elements in the tailings. The XRF machine was calibrated against XRF standards prepared by SGS Laboratory using lithium metaborate fusion/ICP-AES.

2.4.7 Non-sequential Chemical Extractions

Non-sequential chemical extractions were performed on sampled cores to characterize metal(loid)s associated with various secondary phases at Parc B of Mine Principale. The chemical extraction procedures targeted the following phases: water-soluble phases, insoluble sulfates, amorphous oxyhydroxides, poorly crystalline phases and carbonates, and all reducible phases (Table 2.3). Water-soluble fraction were targeted using deionized (DI) water purged with argon gas for about 30 minutes to reduce dissolved O₂ (Ribet et al., 1995; Gunsinger et al., 2006). Insoluble sulfates were targeted using an alkaline solution of 0.3 M NaOH, which usually converts iron oxyhydroxysulfates into iron oxyhydroxides via incongruent dissolution, releasing SO₄ to the solution in the process (Yin & Catalan, 2003). A weak reducing solution of 0.12 M Na-ascorbate, 0.6 M Na-ascorbate and 0.17 M Na-ascorbate, referred to as the ascorbate extraction, was used to target amorphous Fe(III) (oxy)hydroxides (Amirbahman et al., 1998). The ascorbate extraction was done in the dark by wrapping the centrifuge tubes with aluminum foil before putting them on the end-over-end rotator. The chemical extractions by DI, 0.3 M NaOH, and ascorbate were all conducted in the COY anaerobic chamber. A strong reducing solution of 2 M hydroxylamine hydrochloride (NH₂OH.HCl) with 25% (vv⁻¹) acetic acid, commonly abbreviated as 2 M HHCl, was heated at 95⁰C in a pot containing glycerin

to target all reducible phases (Ribet et al., 1995). An acidic solution of 0.5 M HCl was used to target acid-leachable phases (Heron et al., 1994). After 0.5 M HCl extraction, Fe(II) concentrations in supernatants were determined using a HACH[®] spectrophotometer (method 8146 with 1,10 phenanthroline powdered reagent). The concentrations of Fe(III) were determined by subtracting Fe(II) concentrations from the total Fe concentrations that were determined using ICP-OES.

The supernatants were centrifuged after the defined digestion period and filtered with a 0.45 μm membrane. The supernatants for cation analysis were acidified to $\text{pH} < 2$ using 16 M HNO_3 where necessary and analyzed for dissolved metals using ICP-OES (iCAP 6000 by Thermo Fisher Scientific). Cation analysis was performed using ICP-MS (X series II by Thermo Fisher Scientific) to determine the concentrations of trace metal(loid)s that may not be detected by ICP-OES. ICP-MS analysis on supernatants obtained from the ascorbate and 0.5 M HCl extractions was not possible due to high concentrations of other constituents. The supernatants obtained from the DI and the 0.3 M NaOH extractions were also analyzed for SO_4 with ion chromatography. Blank reagent samples were analyzed for any potential contaminations, and over 15% of samples were used as replicates to obtain reproducible results. The results were then compared to powder XRF results.

Table 2.4. Summary of selective chemical extraction steps used to characterize metal(loid)s associated with different phases at Parc B (adapted from Gunsinger et al., 2006).

Target Phases	Reagent	Tailings/ Reagent ratio	Digestion period (h)	Source
Water-soluble phases	Deionized water	1:50	24	Ribet et al. (1995)
Insoluble sulfates	0.3 M NaOH	1:30	16	Yin & Catalan (2003)
Amorphous oxyhydroxides	0.12 M Na-ascorbate, 0.6 M Na-bicarbonate, & 0.17 M Na-citrate	1:20	24 (in dark)	Amirbahman et al. (1998)
Acid-leachable phases	0.5 M HCl	1:10	24	Heron et al. (1994)
Reducible amorphous and crystalline phases	2 M hydroxylamine hydrochloride [NH ₂ OH.HCl] with 25% (vv ⁻¹) acetic acid, abbreviated as 2.0 M HHCl	1:30	24 (at 95°C)	Ribet et al. (1995)

2.4.8 Synchrotron-based Analysis

Synchrotron-based powder X-ray diffraction (PXRD) was performed remotely at the CMCF-BM beamline at the Canadian Light Source (CLS) in Saskatoon, SK. Samples were dried in a COY anaerobic chamber and ground to a fine powder using Wig-L-Bug grinding mill before being put into Kapton (polyimide) capillaries and sealed with Loctite 454 (Prism gel) epoxy. Each capillary was then stored in a sealed cryotube in a freezer at the CLS facility before being put into CMCF staff-approved sample containers for remote data collection. During remote data collection, samples were loaded onto B3S-Reusable bases and loaded into the automounter, and the sample holder was then oriented at 90° to the beam and centered, with the energy of the beamline adjusted to 18 keV, which is the standard energy for PXRD analyses on the CMCF beamlines. After running a test spectrum to ensure that beamline parameters were optimal, multiple XRD spectra were then collected for each sample. At the start of the shift, a blank Kapton tube was run. Data was calibrated and integrated using GSASII, and peaks were identified using PDF-4+ and sieve+. Another synchrotron-based μ -XRF and micro-X-ray absorption near-edge structure (μ -XANES) analyses were conducted remotely at the Advanced Photon Source (APS) (beamline 20-ID-B, C) Chicago, Illinois, to determine elemental distributions and Fe speciation in the rims of weathered sulfide minerals, respectively. The iron data, however, was too noisy to be utilised in the processing of iron speciations. Data processing and analysis of μ -XRF maps were completed using PyMca software, which is a stand-alone application for analysis of X-ray fluorescence spectra.

2.4.9 Microbiology

2.4.9.1 Sampling for Microbiological Study

Samples for microbiological study were collected at the site using thin-walled aluminum tubing of 5.08 cm (2 in) in diameter, cut into lengths of about 40 cm sub-cores and immediately placed in a freezer. A core splitter (Craftsman) was then used to split the cores lengthwise while frozen. One split of each core was immediately wrapped in plastic paper and electrical taped at the ends before being returned to the freezer for future use, and the other one was allowed to thaw overnight at room temperature (25°C) inside a COY anaerobic chamber before the collection of samples for microbiological study was carried out lengthwise based on visual changes. Samples were taken from the centre of the split to minimize samples contamination. Microbial DNA extraction was performed, as per the steps outlined in Qiagen DNeasy PowerSoil Kit (Cat No./ID: 47014).

2.4.9.2 DNA Extraction, PCR Amplification, and Illumina MiSeq Sequencing

Prokaryotic populations were analyzed using high-throughput amplicon sequencing of 16S rRNA genes (details provided in Pakostova et al., 2020b). In short, DNA was extracted in duplicate from the sub-samples (stored at -20°C) using DNeasy PowerSoil Kits (Qiagen Inc., Germany), following the manufacturer's instructions. Quality DNA was stored at -20°C and submitted to Metagenom Bio Inc. (Waterloo, Canada). The PCR amplification of the V4 region of 16S rRNA genes was performed using the modified universal primers 515F/806R (Walters et al., 2015) prior to Illumina MiSeq sequencing.

2.4.9.3 Illumina Sequence Data Processing

Sequence data were analyzed using the mothur program v.1.39.5 (updated: 3/20/2017; Schloss et al., 2009), and the MiSeq SOP (Kozich et al. 2013; https://www.mothur.org/wiki/MiSeq_SOP) from 20/08/2021. Six out of total 30 samples which contained fewer than 7,300 sequences were removed. A detailed description of sequence data processing can be found in Pakostova et al. (2020b). In short, chimeric sequences were discarded based on predictions by vsearch using the Silva database for 16S rRNA gene sequences (release

132 for mothur, downloaded 18/03/2019) as a reference. Sequences were clustered into OTUs (operational taxonomic units) at a 97% similarity level by a de novo picking method. Taxonomic annotation of individual OTUs was based on mothur-formatted version of the Silva reference database. Several taxa (unknown, mitochondria, eukaryotes) were not considered for further data analysis. Cyanobacteria were kept for further processing.

Good's coverage was used to assess how representative the samples were of the environments from which they were taken. The Gini-Simpson's diversity index (1-D) and Chao1 richness estimator were chosen to measure the microbial α -diversity for each library. β -diversity was investigated using UniFrac (Lozupone and Knight, 2005), and visualized using 3D non-metric multidimensional scaling (2D-NMDS). The analysis of molecular variance (AMOVA) was used to determine whether the diversity within a group was greater than their pooled diversity. Relative abundances of sulfate-reducing bacteria (SRB), iron-oxidizing (IOM), and sulfur-oxidizing (SOM) microorganisms were obtained by screening the taxonomy file for prokaryotic genera (or in a few instances higher taxa when identification to the genus level was not possible) containing at least one species with the investigated metabolic trait.

2.5 Results and Discussion

2.5.1 Sulfide-mineral Oxidation

2.5.1.1 Proximal Area

Gaseous oxygen was recorded below the impoundment surface in the area proximal to the point of tailings discharge in Parc B. The measured pore gas-phase O₂ concentrations were near atmospheric levels and the total sulfur content was low in the top 0.5 mbgs of the tailings (Figure 2.3), which was the depth at which Quantek portable meter and steel drive-point gas rod could manually be inserted into the tailings walls to measure gas-phase O₂. The O₂ concentrations, however, show a downward trend below the depth of 0.5 mbgs that reflects O₂ consumption by sulfide mineral oxidation. An ochreous-colored hole, exceeding 0.8 mbgs in depth, shows the extent of sulfide-mineral oxidation in this zone (Figure 2.4). Oxidant transport is more pronounced in the area proximal to the point of tailings discharge compared to the distal area, primarily due to two contributing factors: 1) the relatively coarse nature of the tailings, and 2) low moisture content that allow greater O₂ diffusion into the tailings, resulting in relatively extensive sulfide-mineral oxidation (Gunsinger et al., 2006). Concentrations of pore gas-phase CO₂ are insignificant above 0.5 mbgs, suggesting that carbonate minerals are depleted by acid-neutralizing reactions. Carbon dioxide concentrations increase below the depth of 0.5 mbgs indicating that carbonate minerals are neutralizing acidity being generated by sulfide-mineral oxidation in the proximal zone (Figure 2.3).

Qualitative observations of sulfide-mineral oxidation conducted based on sulfide alteration indices (SAI) developed by Jambor (1994) also confirm the degree of sulfide minerals weathering in the proximal zone (Figure 2.3). The SAI is a numerical scale that shows the relative degree of alteration of sulfide mineral grains through a tailings depth profile. The scale is based on optical microscopic analysis, where samples are assigned numbers from 1-10, with 10 representing the most extensive sulfide alteration while 1 representing the least sulfide alteration. The SAI is based on the degree of pyrrhotite alteration since pyrrhotite is more susceptible to alteration than other sulfide minerals (Lindsay et al., 2015). Examples of sulfide grains with different degrees of alterations are provided in Figure 2.5. Sulfide minerals ranged from pyrrhotite grains

with thick rims of secondary weathering products to very thin rims along grain boundaries in the transition zone, which was between 1.1 and 1.4 mbgs deep in the proximal zone. The active oxidation front was estimated to be at a depth of about 1.4 mbgs based on SAI data. The averaged sulfide content of the unoxidized tailings was determined to be 5.5 wt.% in the unoxidized zone and 1.9 wt.% in the oxidized zone.

2.5.1.2 Distal Area

No recordings of pore gas-phase O₂ and CO₂ were made in the field because the distal zone was extremely wet at the time of sampling. However, field/laboratory observation and mineralogical study show that sulfide oxidation is limited to areas above 0.35 mbgs. An area characterized by orange/brown tailings, for instance, was observed specifically in the zone above 0.35 mbgs while splitting the cores into halves for sampling in the laboratory. Optical microscopic analyses indicate that pyrrhotite alteration was confined to the surface, while pyrite and chalcopyrite showed little to no signs of weathering. The averaged sulfide content of the unoxidized and oxidized tailings are 3.4 and 2.2 wt.%S, respectively (Figure 2.6). The limited extent of sulfide-mineral oxidation, which can be attributed to the fine texture and high moisture content of the tailings, implies that sulfide-mineral oxidation processes are in the early stages of development in the distal zone.

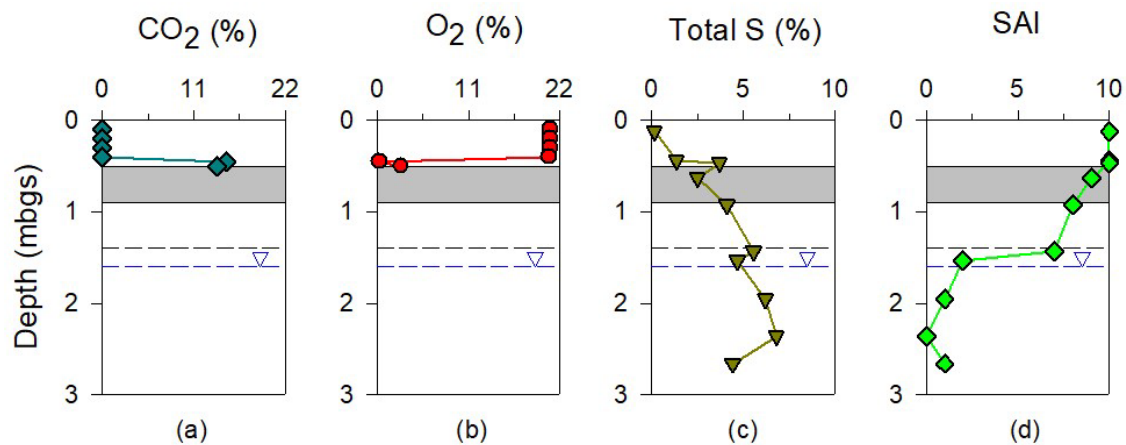


Figure 2.3. (a) Measured concentrations of gas-phases CO₂, (b) measured concentrations of gas-phase O₂, (c) total sulfur content, and (d) Sulfide Alteration Index for Mpr20-6 samples (2020). Dashed line with inverted triangle represents the water table and the shaded grey area represents the hardpan. Dashed line above the water table represents transition zone. Water table depth was estimated on collection of water in the cored holes.

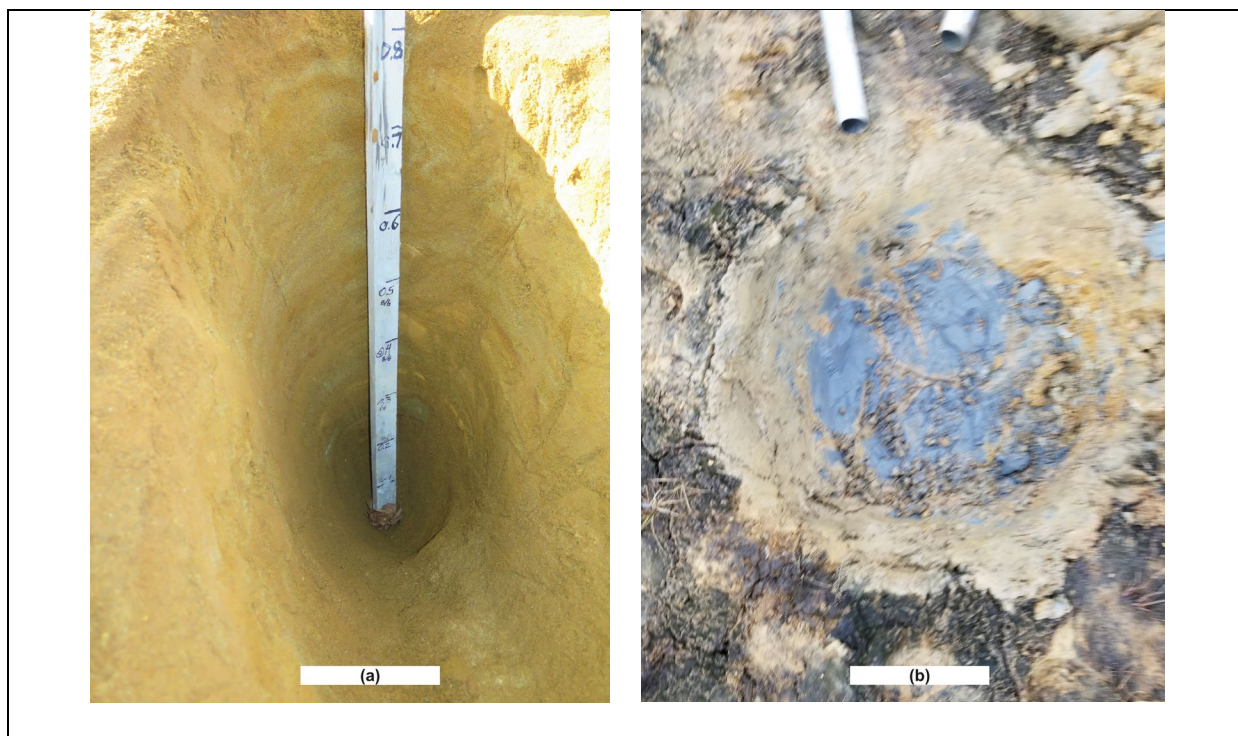


Figure 2.4. Sulfide-mineral oxidation depths in the proximal zone (a) and distal zone (b) (2020).

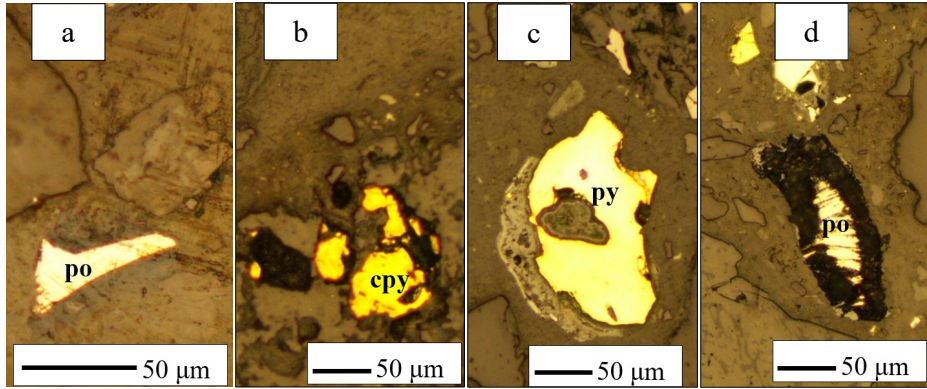


Figure 2.5. Examples of pyrrhotite (a and d), pyrite (c), and chalcopyrite grains (b) from the tailings profile undergoing oxidation in the proximal zone. Reflected light images are organized in order (a, b, c, d) from the least weathered (a) to the most weathered grain (d) (2020).

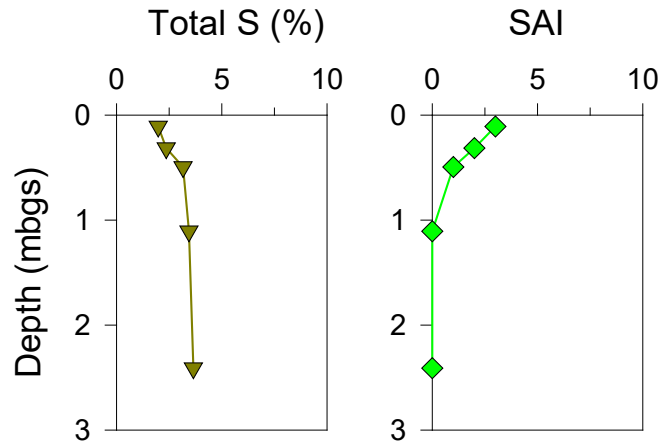


Figure 2.6. Left: Total sulfur content of Mpr20-4 samples. Right: Sulfide Alteration Index for sulfide minerals of Mpr20-4 samples in 2020.

2.5.2 Solid-phase Geochemistry

The abundance of elements in the tailings based on powder XRF analysis follows the order $\text{Si} > \text{Al} > \text{Fe} > \text{Ca} > \text{Mg}$ in both proximal zone (Figure 2.7) and distal zone (Figure 2.8). The order of abundance is in accordance with the mineralogy of the tailings, which consists primarily of quartz, plagioclase, chlorite, pyrite, and pyrrhotite comprising the bulk of the host rock and ore (Table 2.5). Other elements present in insignificant quantities such as MnO and TiO_2 are featured in plots presented in the appendix section (Figure 0.01 and Figure 0.02).

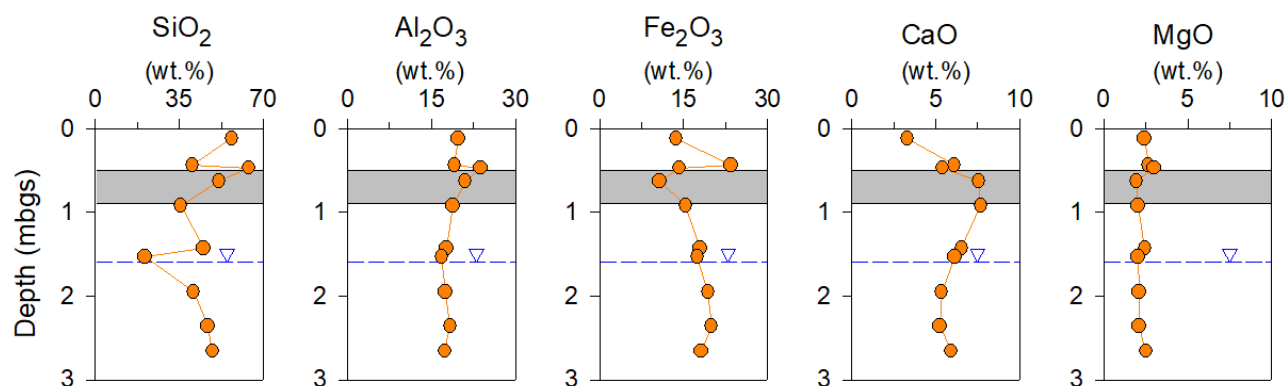


Figure 2.7. Depth profiles of Al₂O₃, Fe₂O₃, CaO, and MgO for Mpr20-6 (2020). Dashed line with inverted triangle represents the water table and the shaded grey area represents the hardpan. Water table depth was estimated on collection of water in the cored holes.

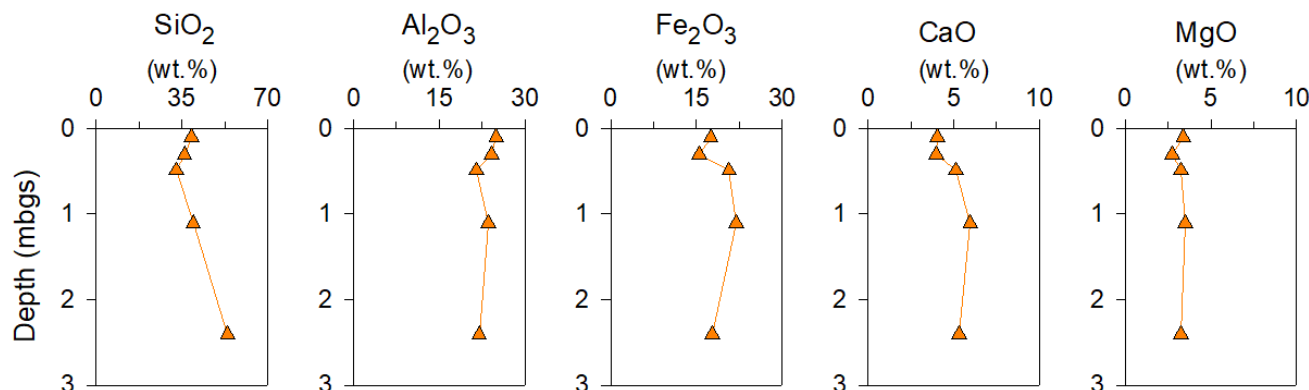


Figure 2.8. Depth profiles of Al₂O₃, Fe₂O₃, CaO, and MgO for Mpr20-4 (2020).

The abundance of trace metal(loid)s in the tailings follows the order $\text{Cu} > \text{Co} > \text{Zn} > \text{As} > \text{Ni} > \text{Pb}$. Powder XRF values for copper and Co were both found in average concentrations greater than $350 \mu\text{g/g}$, whereas Ni, Zn, and As were found in average concentrations less than $350 \mu\text{g/g}$ but greater than $240 \mu\text{g/g}$. Lead has an average concentration lower than $50 \mu\text{g/g}$. The concentrations of Cu, Ni, Zn, and Co generally increase with depth. Arsenic and Pb have average concentrations of $270 \mu\text{g/g}$ and $45 \mu\text{g/g}$, respectively, and their concentrations increase sharply from the top of the tailings to the hardpan layer, then gradually increase beneath the hardpan layer. The average concentration of Cd is $1.4 \mu\text{g/g}$, and it remains relatively steady with depth while that of Cr decreases with depth and its average concentration is $30 \mu\text{g/g}$ (Figure 2.9 & Figure 0.03). Trace elements in the distal zone follow similar trends and are plotted on Figure 0.04 in the appendix section.

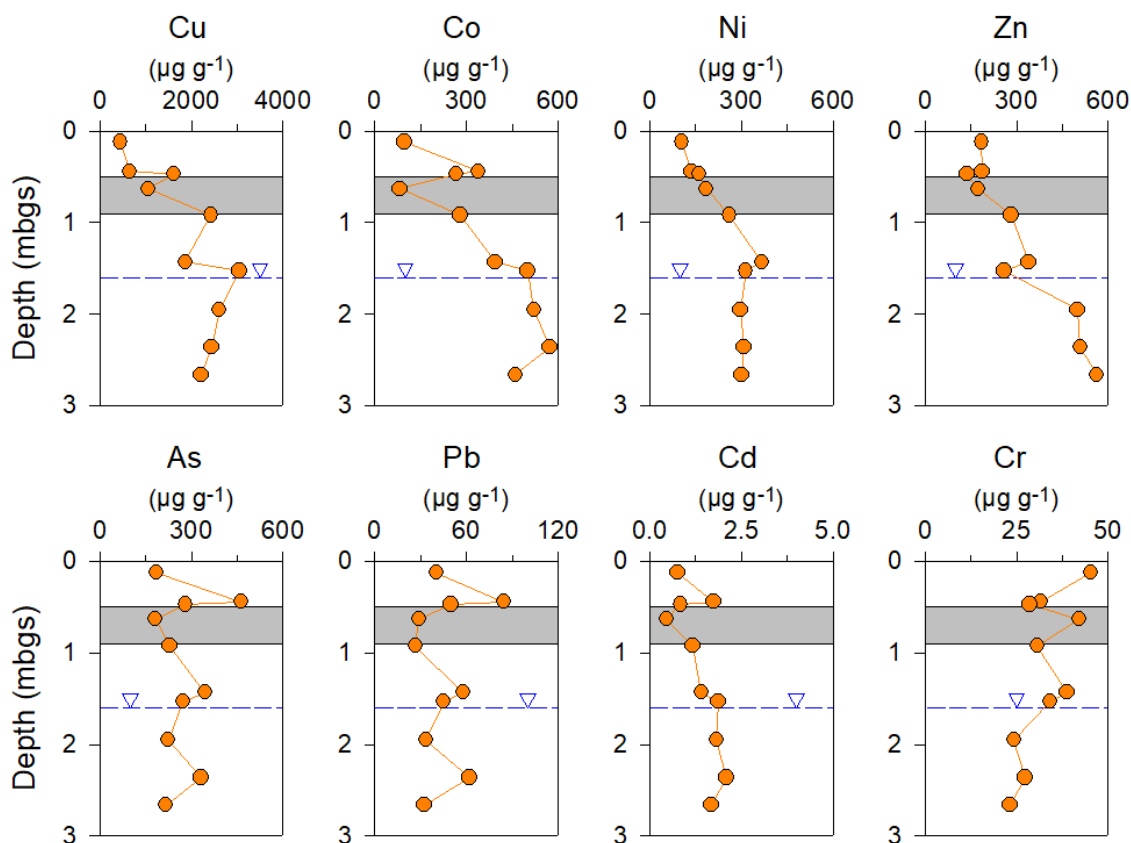


Figure 2.9. Depth profiles of trace metal(loid)s Cu, Co, Ni, Zn, As, Pb, Cd, and Cr for Mpr20-6 (2020). Dashed line with inverted triangle represents the water table and the shaded grey area represents the hardpan. Water table depth was estimated on collection of water in the cored holes.

Table 2.5. Common minerals observed in Parc B tailings.

Mineral group	Common minerals detected with optical microscopy/XRD
Sulfides	Pyrrhotite, pyrite, chalcopyrite, sphalerite, pentlandite
Aluminosilicates	Chlorite, feldspar
Oxides	Quartz, Fe oxyhydroxides, hematite
Carbonates	Calcite, dolomite-ankerite
Others	Gypsum, jarosite

Sulfide grains from different depths were analyzed with SEM-EDS and synchrotron-based μ -XRF elemental mapping to determine the presence of hazardous metal(loid)s within the alteration rims of sulfide minerals, particularly pyrrhotite mineral that is high susceptible to weathering compared to other sulfide minerals. Alteration rims of weathered pyrrhotite grains were mapped to determine the presence of hazardous metal(loid)s. Elemental distribution maps in Figure 2.10 show that elements including Ni and Co are highly concentrated in the alteration rims of weathered pyrrhotite.

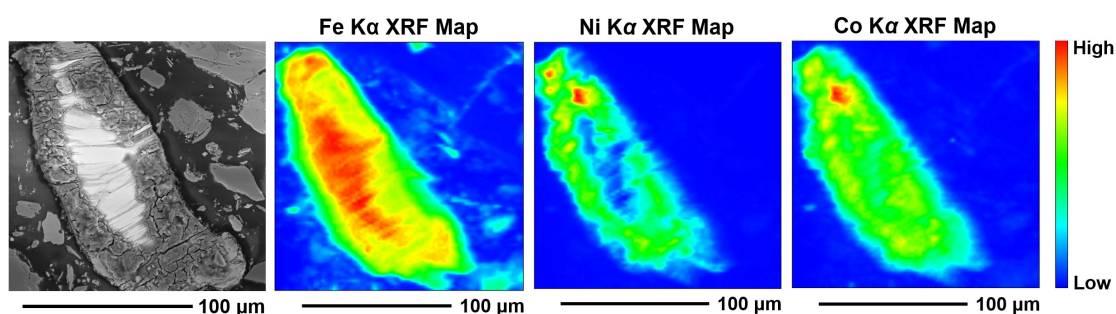


Figure 2.10. SEM image of the pyrrhotite $[\text{Fe}(1-x)\text{S}]$ sulfide minerals from a depth of 1.4 mbgs in the tailings profile with visible weathered rims (dark grey) of Fe (oxy) hydroxides. Nickel and Co μ -XRF elemental distribution maps showing high concentrations in the alteration rims of a weathered pyrrhotite (2020).

2.5.3 Aqueous Geochemistry

The extensive sulfide-mineral oxidation within Mpr20-6 compared to Mpr20-4 has resulted in low pH conditions (2.5 – 4.0), which gradually increases to more than 7.0 at the depth of 3.1 mbgs. Sulfide-mineral oxidation has led to elevated concentrations of SO_4 (up to 12000 mg L^{-1}) and Fe (up to 1,800 mg L^{-1}), and significant accumulations of toxic metal(loid)s including Cu (up to 100 mg L^{-1}), Ni (up to 20 mg L^{-1}), and Zn (up to 7.0 mg L^{-1}). Their concentrations mostly peak in the hardpan layer and decrease from the transition zone to the unoxidized zone underneath it (Figure 2.11). The pore-water chemistry for 2020 is located in Appendix A.

The pH values steadily decrease from the surface of the tailings to the hardpan layer before gradually increasing to circumneutral pH values at depths. The lowest recorded pH value (2.5) was observed within the hardpan layer at a depth of 0.6 mbgs. The H^+ generated by sulfide-mineral oxidation in mine tailings is consumed by acid-neutralizing reactions involving carbonates, oxyhydroxides, and silicates (McGregor et al., 1998; Coggans et al., 1999; Lindsay et al., 2015). Saturation indices were calculated for pore-water samples with pH values greater than 4 and measurable alkalinity (Figure 2.12). The results of geochemical modelling with PHREEQCi indicate that pore-water is saturated with respect to calcite and siderite at depths below 2.4 mbgs. Mineralogical study with XRD confirmed the presence of calcite but not that of siderite.

Sulfate and Cl are the major anions in the pore-water with the maximum concentrations of 12000 mg L^{-1} and 17.5 mg L^{-1} , respectively. Sulfate concentrations greater than 1500 mg L^{-1} persist to a depth of 3.1 mbgs. The oxidation of sulfide minerals, mainly pyrite and pyrrhotite, are the main sources of SO_4 in the pore-water. Solid-phase analyses indicate that the sulfide content in the unoxidized tailings varies between 3.4 wt% in the area distal to the point of tailings discharge (Mpr20-4) to approximately 10.6 wt% in the area proximal to the point of tailings discharge (Mpr20-6). Disposal of tailings from multiple separate sources and hydraulic sorting during discharge can probably explain this observed disparity in sulfide content between the proximal and distal zones. Geochemical modelling indicates that all pore-water in the depth

profile is at or near equilibrium with respect to gypsum. The mine-process water and the gangue minerals dissolution acted as potential sources of Ca necessary for the formation of gypsum. The concentrations of Cl and Na follow similar trends suggesting sodium chlorite as the likely source. The pore-water is undersaturated with sodium chloride, but it was detected during the XRD analysis. Other anions that were measured included fluoride, nitrite, bromide, nitrate, and phosphate. The concentrations of fluoride, nitrite, bromide, and phosphate are less than 0.1 mg/L while the concentration of nitrate (2.0 mg/L) is restricted to the top of the tailings suggesting plant remains as the likely source.

Major cations in Parc B include Ca, Al, Mg, Fe, Cu, Ni, Co, and Zn. The oxidation of pyrrhotite and pyrite and other sulfide minerals by O₂ or Fe(III) releases Fe(II) to the pore-water. Measured pore-water concentrations of Fe reached a maximum of 1800 mg L⁻¹ at a depth of 0.6 mbgs, which coincide with a pH value of 2.5. Dissolved Fe concentrations decrease rapidly below a depth of 3.1 mbgs in Mpr20-6. The solubility of Fe is controlled by pH, changing redox conditions and the precipitation of Fe(III) (oxy)hydroxides and hydroxysulfates (Lindsay et al., 2015). Geochemical modelling of the groundwater suggests that precipitation of secondary Fe(III) (oxy)hydroxides and hydroxysulfates control the concentrations of dissolved Fe. The pH values increase approximately to 7.4 at a depth of 3.1 mbgs as the concentration of dissolved Fe decreases.

The concentration of Ca decreases near the hardpan layer but is constant within and below the hardpan layer. Hardpan layers generally contain gypsum (Blowes et al., 1990; Moncur et al., 2005; Lindsay et al., 2015). The dissolution or precipitation of gypsum could act as a source or sink of Ca. Other potential sources of Ca include milling reagents and Ca derived from the dissolution of carbonate and alumino-silicate minerals (Coggans et al., 1999).

The dissolution of aluminosilicate minerals releases Al into the tailings pore-water. Below pH 5.5, the pore-water becomes strongly undersaturated with respect to calcite, dolomite and siderite, and dissolved Al concentration rises markedly. Similar observations have been reported in waters affected by acidic drainage from sulfidic tailings (Dubrovsky et al., 1985; Blowes and Jambor, 1990). At all of these sites, the

increase in Al has been attributed to the dissolution of aluminosilicate and/or aluminum hydroxide minerals. Mineralogical examinations indicate weathered grains of aluminosilicate minerals such as albite exist within the tailings. As the pH rises to approximately 7, the concentration of Al drops sharply. Magnesium reached maximum concentrations of 250 mg L^{-1} within the hardpan layer. The dissolution of aluminosilicate minerals is the main source of Mg observed in the pore-water.

The oxidation of chalcopyrite is the primary source of dissolved Cu in the pore-water. Concentrations of Cu in the tailings reached a maximum of 100 mg L^{-1} within the upper part of the hardpan (0.6 mbgs), then quickly drop to less than 0.02 mg L^{-1} at the depth of 2.0 mbgs. Geochemical modelling shows that pore-water is undersaturated with respect to all other Cu-bearing secondary minerals in the WATEQ4F database, including covellite.

Nickel is likely released to the pore-water by the oxidation of nickel-bearing pyrite and pentlandite. Pentlandite was observed with XRD, and traces of Ni were observed on unoxidized pyrite grains in SEM-EDS analysis. Pore-water concentrations of Ni reached 20 mg L^{-1} at the depth of 1.6 mbgs, suggesting its high mobility in the tailings water compared to other trace metal(loid)s analyzed in this study. Dissolved Co in the pore-water is likely to have been derived mainly by oxidation and dissolution of pyrrhotite and pyrite as traces of Co were detected on unoxidized pyrrhotite and pyrite. The maximum concentrations of dissolved Co detected within the hardpan of Parc B is 40 mg L^{-1} . Chromium is likely released to the pore-water by the oxidation of pyrite since traces of Cr were also detected on unoxidized pyrite grains in SEM-EDS analysis. The maximum concentrations of dissolved Cr in the tailings pore-water is $392 \text{ } \mu\text{g L}^{-1}$. Geochemical modelling indicates that pore-water is undersaturated with respect to all Ni-, Co-, and Cr-bearing phases in the WATEQ4F database.

Dissolved Zn is derived from the oxidation of sphalerite which was detected during mineralogical analyses. Dissolved Zn concentrations reached a maximum of 7.0 mg L^{-1} in the hardpan layer. These concentrations quickly decrease to below detection limits ($< 0.02 \text{ mg L}^{-1}$) as the pH increases. Geochemical

modelling suggests that pore-water is undersaturated with respect to smithsonite $[\text{ZnCO}_3]$, boyleite $[\text{ZnSO}_4 \cdot 4\text{H}_2\text{O}]$, and amorphous zinc hydroxide $[\text{Zn}(\text{OH})_2]$.

The concentrations of dissolved hazardous metal(loid)s are relatively lower in Mpr20-4 than in Mpr20-6 due to minimal sulfide-mineral oxidation as shown in Figure 0.06 in the appendix section.

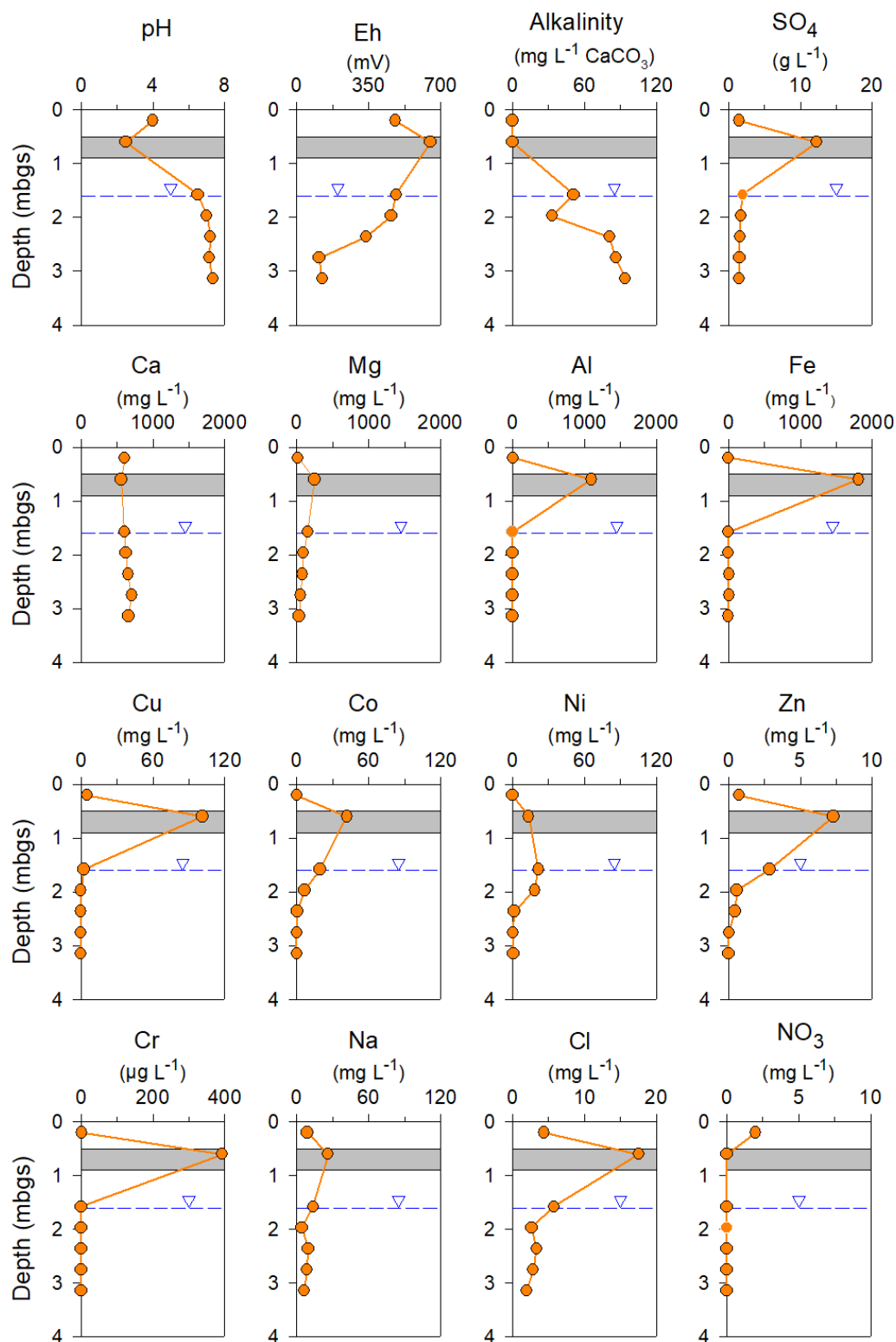


Figure 2.11. Geochemical depth profiles of pH, Eh, Alkalinity, SO₄, Fe, Ca, Mg, Al, Cu, Ni, Co, Zn, Cr, Na, Cl, and NO₃ of Mpr6-20 location for 2020. Dashed line with inverted triangle represents the water table and the shaded grey area represents the hardpan. Water table depth was estimated on collection of water in the cored holes.

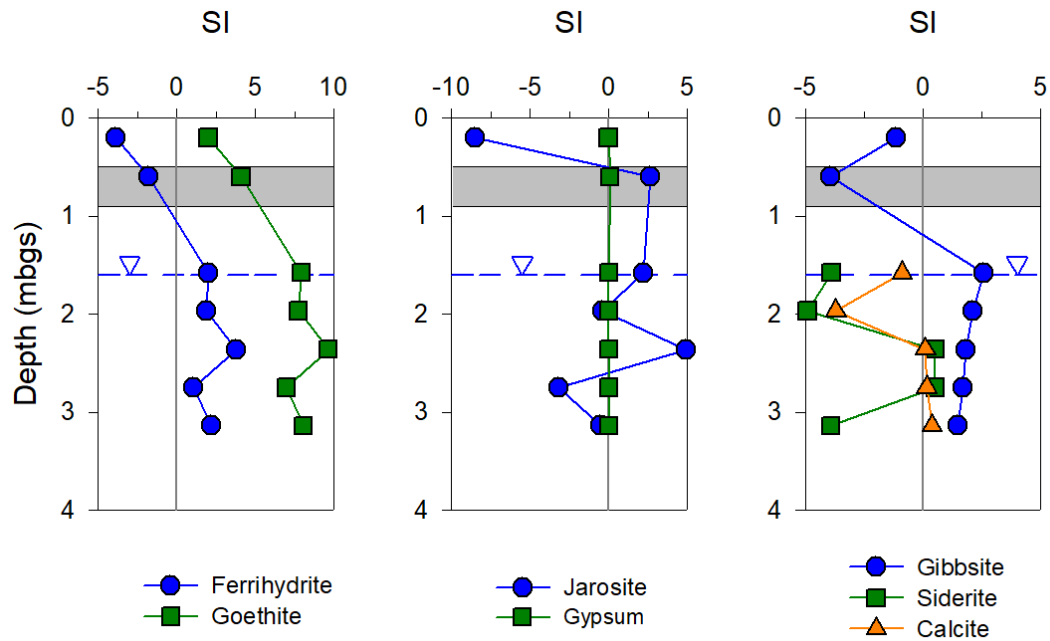


Figure 2.12. Geochemical modelling of saturation indices of mineral phases which potentially control precipitation-dissolution reactions in Parc B tailings of Mine Principale (2020). Dashed line with inverted triangle represents the water table and the shaded grey represents the hardpan. Water table depth was estimated on collection of water in the cored holes.

2.5.4 Selective Chemical Extractions

A series of selective, non-sequential chemical extractions was conducted to assess the potential release of hazardous metal(loid)s, including Fe, Cu, Ni, and Zn, into the environment following the application of the proposed EWT technique (Figures 2.13 – 2.14, and Figures 0.09 – 0.12 in Appendices). The chemical extraction steps targeted water-soluble phases, insoluble sulfates, amorphous oxyhydroxides, poorly crystalline phases and carbonates, and all reducible phases. Water soluble and insoluble sulfate phases account for less metal(loid)s compared to amorphous oxyhydroxides, weakly crystalline phases and carbonates, and all reducible phases. Concentrations of metal(loid)s vary across the depth profile of the tailings, with the majority of metal(loid)s found in the oxidation and transition zones, where sulfide-mineral oxidation and subsequent release of metal(loid)s to the pore-water, have occurred.

The results of water-soluble phases indicate that gypsum [CaSO_4] is the only soluble secondary phase associated with most metal(loid)s in the oxidized tailings. The water-soluble Ca and SO_4 depth profiles are similar throughout the depth profile. Melanterite [$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$] and rozenite [$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$] are two other water-soluble secondary phases that could be linked to the Fe peak observed between the hardpan layer and transition zone (Blowes et al., 1991; Moncur et al., 2005).

The results of insoluble sulfates suggest that these phases do not contain a significant amount of toxic metal(loid)s, with the exception Cu and Ni, which have peaks above the hardpan layer. Jarosite [$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$] could be the host for these two trace elements (Blowes et al., 2014).

The ascorbate extraction targeted amorphous oxyhydroxide phases, such as amorphous Fe(III) (oxy)hydroxides and ferrihydrite. The maximum concentration of Fe, which is the dominant element in these phases, was observed in the transition zone above the water table. The distribution of Cu was observed to follow the Fe trend, suggesting that they are co-precipitated with amorphous oxyhydroxide phases (Mcgregor et al., 1998; Gunsinger et al., 2006).

The 0.5 M HCl extraction targeted acid-leachable phases such as carbonate minerals and poorly crystalline Fe(III) (oxy)hydroxides such as goethite. In the oxidized tailings, the distribution of metal(loid)s

including Cu and Ni follows the Fe trend, implying that they are potentially co-precipitated with weakly crystalline oxyhydroxide phases.

The final extraction was adapted from Gunsinger (2006), and it targeted a reducible fraction that includes amorphous to poorly-crystalline oxide phases, jarosite, and poorly-crystalline sulfide phases. The results of this step indicate that maximum concentrations of Fe were observed in the shallow tailings above the hardpan layer. The high Fe concentrations in this zone are attributable to more extensive sulfide-mineral oxidation that has nearly obliterated pyrrhotite, resulting in the formation of goethite, sulfur, and jarosite. Copper follows Fe trend observed in this study. Copper concentrations are high in the transition zone, suggesting that the dissolution of covellite [CuS] by 2.0 M H₂SO₄ is releasing Cu into the solution. Zinc and Ni slightly follow Fe trend in the shallow tailings but increase in concentrations at depths, suggesting that sphalerite and Ni-bearing pyrrhotite are being dissolved by the strong acidity of 2.0 M H₂SO₄.

The low concentration of metal(loid)s in the distal zone (Figures 0.13 – 0.16 in the appendices) is attributed to the limited oxidation of sulfide minerals, which is a consequence of the presence of fine-textured materials and elevated moisture content.

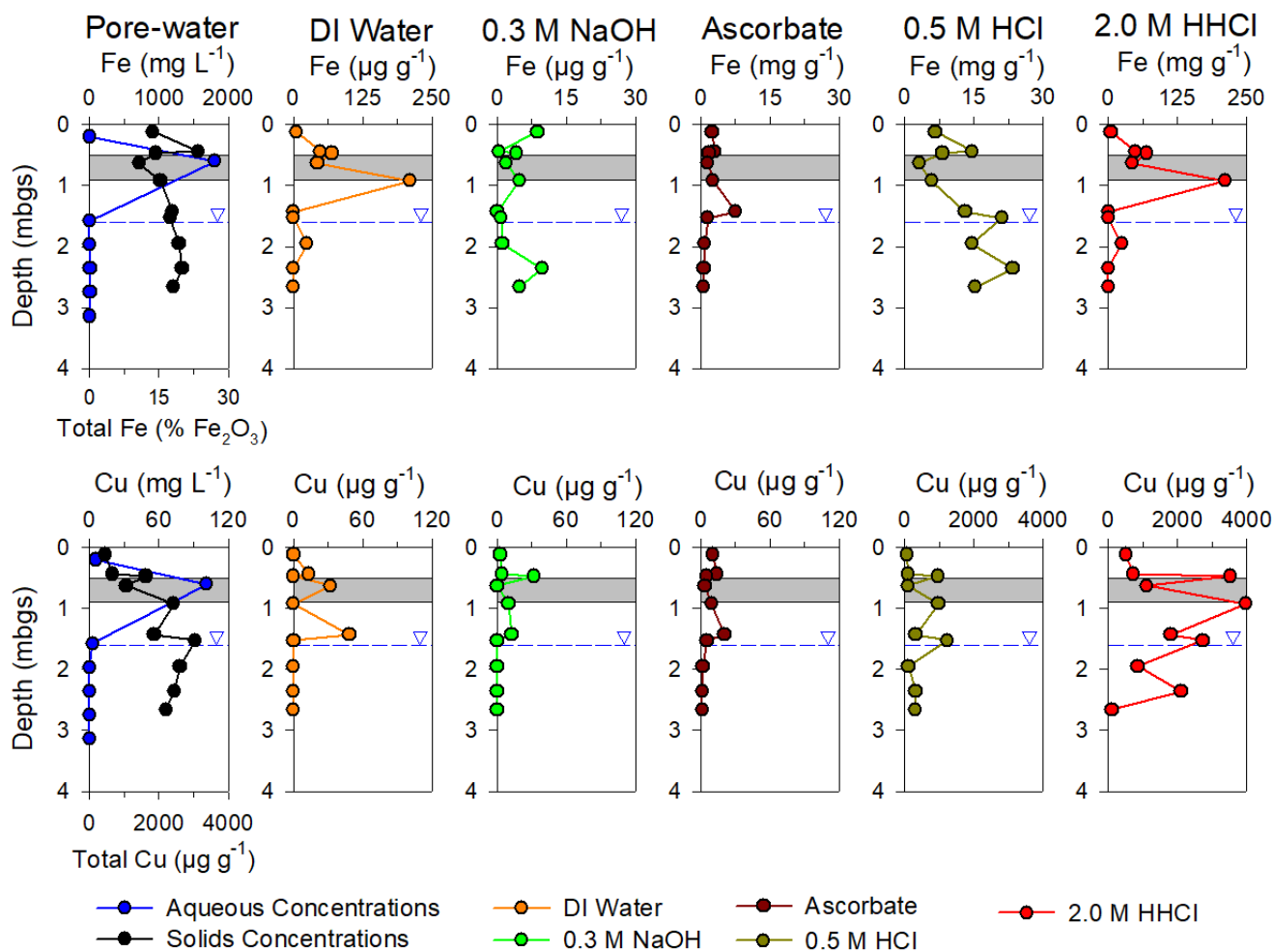


Figure 2.13. Results from selective extractions plotted against depth and geochemical profiles of Fe and Cu (2020). Dashed line with inverted triangle represents the water table and the shaded grey area represents the hardpan. Water table depth was estimated on collection of water in the cored holes.

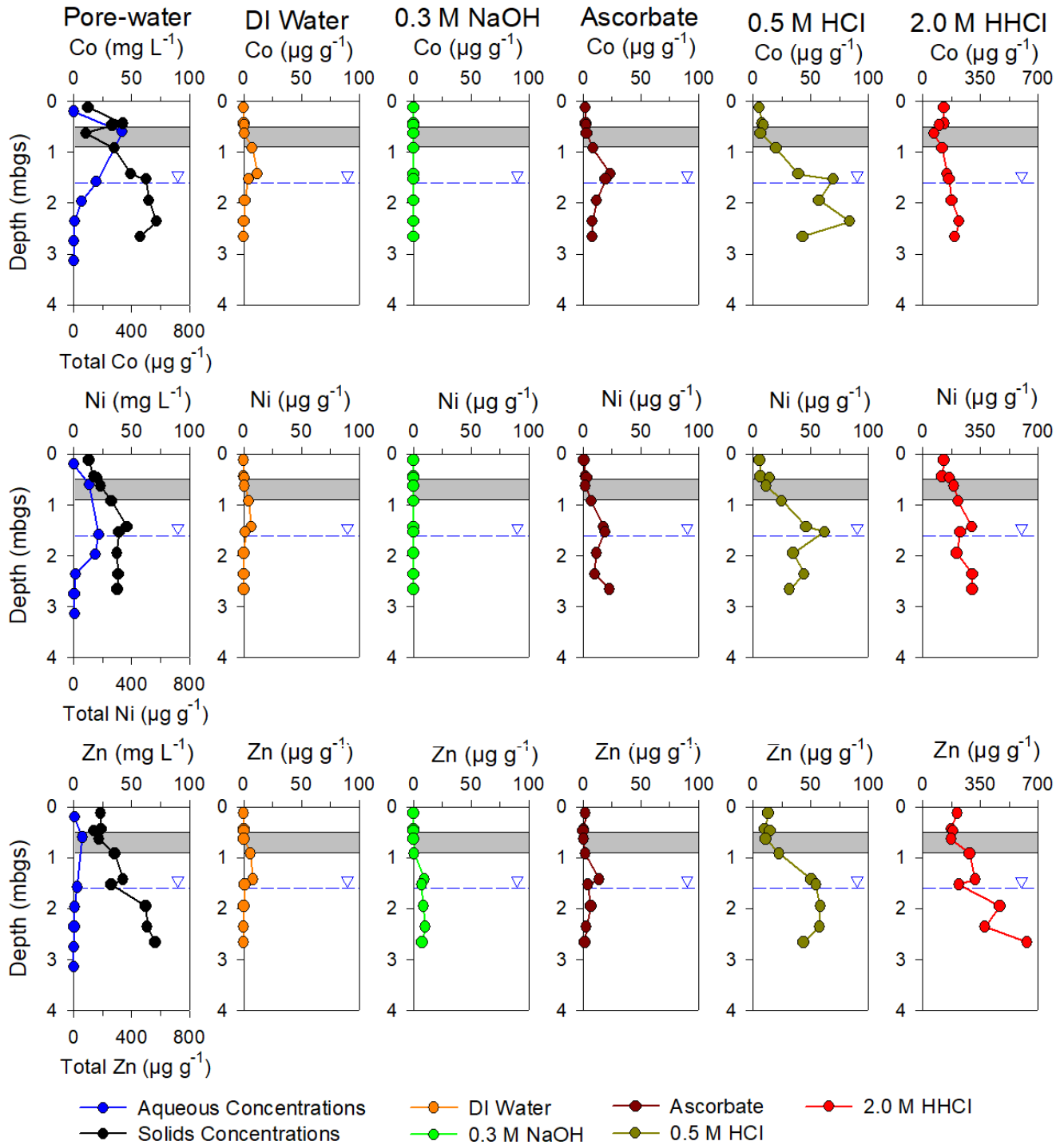


Figure 2.14. Results from selective extractions plotted against depth and geochemical profiles of Co, Ni, and Zn (2020). Dashed line with inverted triangle represents the water table and the shaded grey area represents the hardpan. Water table depth was estimated on collection of water in the cored holes.

2.5.5 Microbiology

2.5.5.1 Overview of 16S rRNA Gene Sequence Data Statistics

In total 816,175 raw sequence reads were obtained, with an average of $34,007 \pm 3,996$ reads per sample (mean $\pm$ standard error; confidence level 95%). About 8.78% of sequences were lost during quality trimming. A total effective sequence number was 744,536 with $31,022 \pm 3,652$ reads per sample, and an average of 202 ± 24 OTUs (97% sequence similarity) per library. Good's coverage (calculated for an OTU definition of 0.03) ranged from 98.4 to 99.7%. Sequence data statistics are summarized in Table 0.1 in Appendices.

2.5.5.2 Entire Bacterial and Archaeal Communities

Proteobacteria were the most abundant phylum in most samples (mean relative abundance 33.3% of the total reads), followed by Firmicutes (10.2%), Actinobacteria (9.6%), WPS-2 (7.3%), Patescibacteria (5.4%), and Chloroflexi (5.2%) (Figure 2.15). The phyla Proteobacteria and Firmicutes contain many species that catalyze the dissimilatory oxido-reduction of iron and/or sulfur. Mean relative abundance of unclassified bacteria on the phylum level accounted for 9.0% of the total amplicons. Archaeal DNA constituted for only 1.5% of the total amplified 16S rRNA genes.

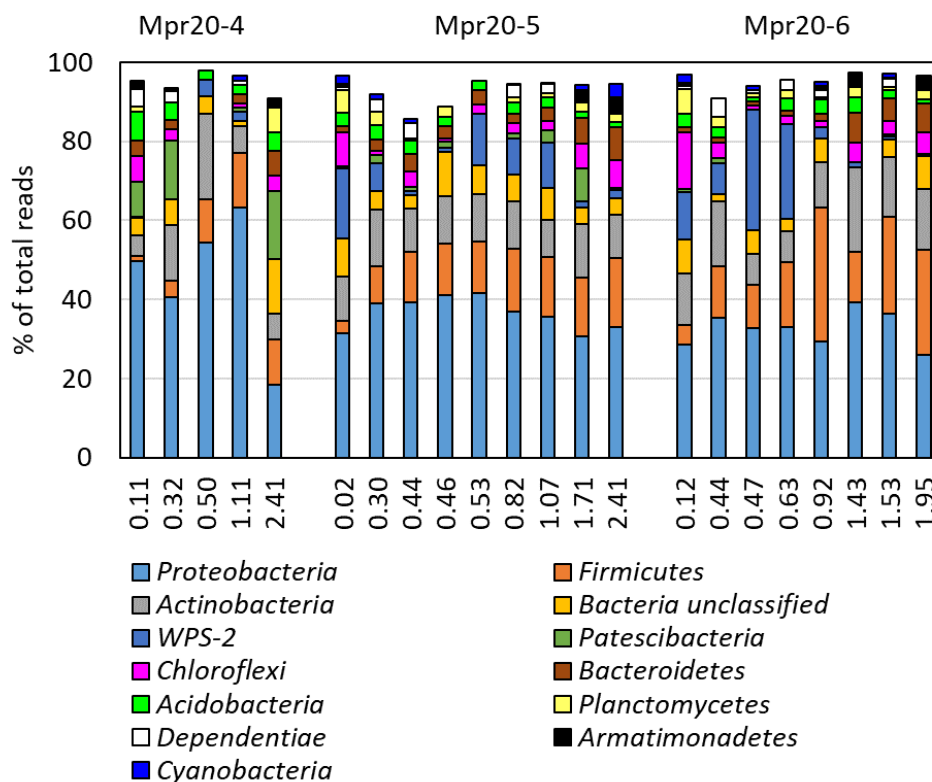


Figure 2.15. Proportions of total reads of major phyla (relative abundance >1.0% of total reads).

Major genera (or higher taxa when identification to the genus level was not possible) are shown in Table 0.2. Minor genera (<0.5% of total amplicons) were grouped together, and their sum accounted for 52.8% of total reads. The most dominant prokaryotic groups could not be identified on the genus level (bacteria accounted for 8.9%, WPS-2 for 7.3%, Proteobacteria for 2.6%, and Gammaproteobacteria for 2.5% for total reads). The most abundant groups that could be identified on the genus level were the pathogenic *Pseudomonas* (1.7%), sulfate-reducing *Desulfosporosinus* (1.2%), and sulfur- and iron-oxidizing *Acidithiobacillus* (0.9%) (Figure 2.17).

A 2D-NMDS plot (based on weighted UniFrac) in Figure 2.16 shows the comparison of bacterial and archaeal communities (BACs) in the analyzed samples. Significant differences (AMOVA, $P < 0.05$) in β -diversity were found between BACs in samples from Mpr20-4 and Mpr20-5, and also between BACs in Mpr20-4 vs. Mpr20-6. In other word, the only insignificant difference was observed between BACs in samples from Mpr20-5 and Mpr20-6. Similar results were obtained with unweighted UniFrac (Figure 0.17 in Appendices). The significance variation in β -diversity between Mpr20-4 and the other sample locations (Mpr20-5 and Mpr20-6), which have similar β -diversity differences, confirms the observed differences in extent of sulfide-mineral oxidation between more oxidized tailings (Mpr20-5 & Mpr20-6) and less oxidized tailings (Mpr20-4), since microorganisms often occupy specific niches within an environment based on factors such as temperature, pH, and available nutrients (Blowes et al., 2014).

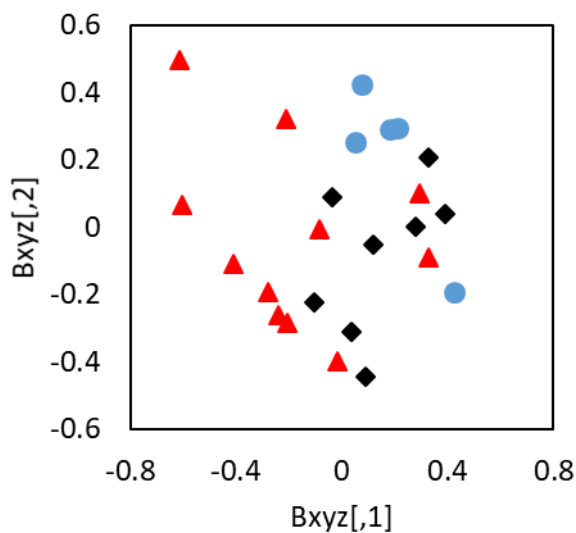


Figure 2.16. 2D-NMDS plot (stress=0.248) of weighted UniFrac used to investigate BACs in (●) Mpr20-4, (▲) Mpr20-5, and (◆) Mpr20-6 samples. The distance between any two points represents the difference between those two communities.

2.5.5.3 Iron- and Sulfur-metabolizing Genera

Figure 2.17 shows the relative abundances of prokaryotes involved sulfur and/or iron biogeochemical cycling.

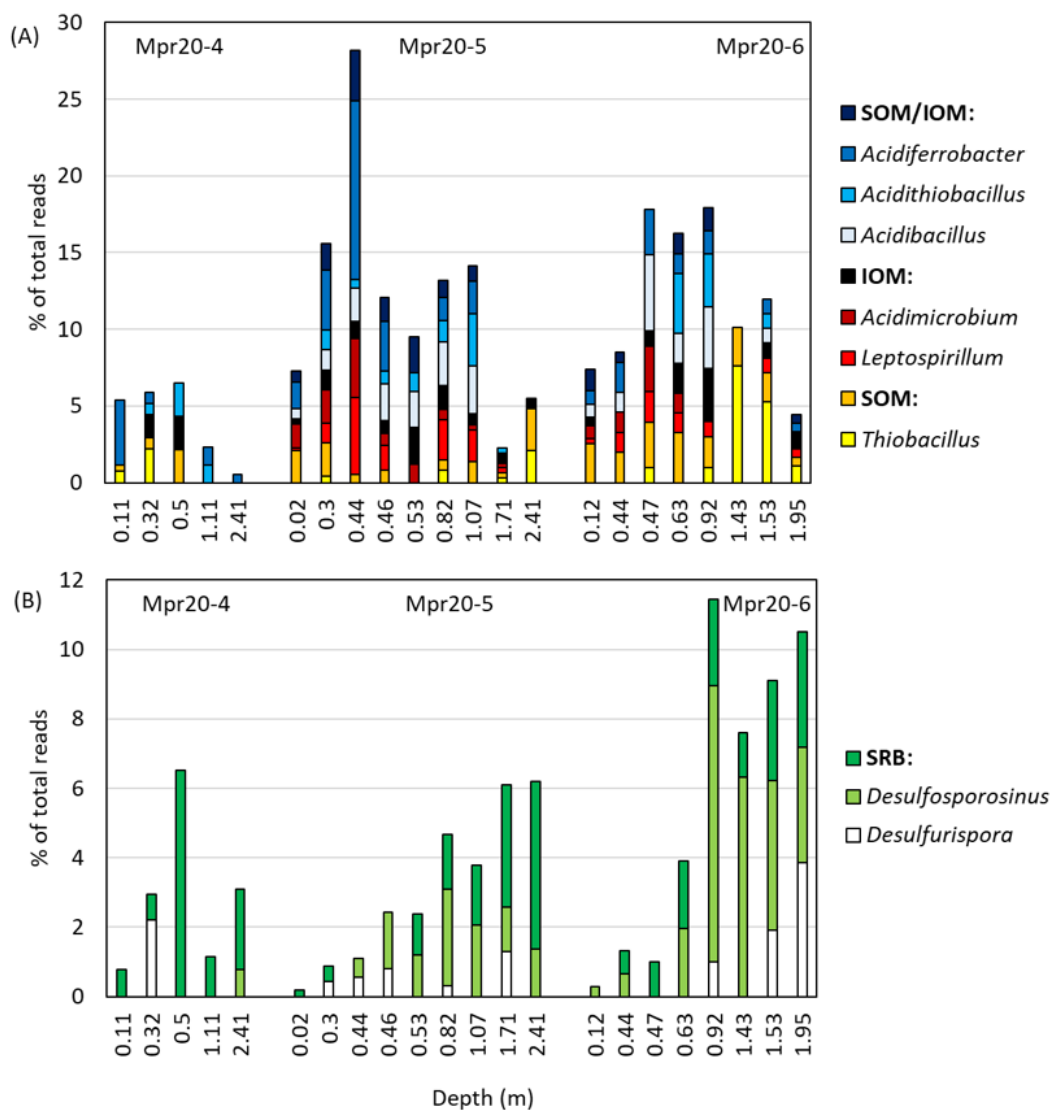


Figure 2.17. Proportions of total reads of (A) sulfur- and/or iron-oxidizing, and (B) sulfate- and/or sulfur-reducing bacteria and archaea (on the genus level).

The total abundance of SOM and/or IOM varied greatly across samples, ranging from 0.5 to 28.2% of total reads. The mean abundance of sulfur-and iron-oxidizing genera was $10.1 \pm 1.39\%$ of the total amplicons (mean $\pm$ s.e.), out of which 7.7% were acidophiles and 2.4% neutrophils. The sulfur- and iron-oxidizing *Acidiferrobacter* (accounting for 1.2% of total reads) and *Acidithiobacillus* (0.9%) were the most abundant genera among the sulfur and iron-oxidizing acidophiles, followed by the IOM *Acidimicrobium* (0.8%). The most abundant neutrophilic groups was the sulfur-oxidizer *Thiobacillus*, accounting for 0.6% of total reads. The mean relative abundance of sulfur- and iron-oxidizers in samples from Mpr20-4 ($4.1 \pm 1.2\%$ of total reads; mean $\pm$ s.e.) was significantly lower (t-test; $P < 0.05$) than those in Mpr20-5 ($12.0 \pm 2.5\%$) and Mpr20-6 samples ($11.8 \pm 1.8\%$). Mean relative abundances of all sulfur- and/or iron-metabolizing genera detected in the samples are summarized in Table 0.3. The abundance of sulfur-and iron oxidizing acidophiles, particularly in Mpr20-5 and Mpr20-6, indicates the prevalence of acidic environments resulting from the ongoing oxidation of sulfide minerals (Figure 2.14 (A)), since they are usually metabolically active in acidic environments impacted by mining activities (Blowes et al., 2014).

Sulfur-reducing bacteria (SRB) are also present in significant quantities in the tailings. For instance, the mean relative abundance of SRB constituted for $4.0 \pm 0.7\%$ of total reads (mean $\pm$ s.d.), ranging from 0.3 to 11.4% across the samples, with *Desulfosporosinus* being the most abundant SRB with a mean abundance of 1.2% of total reads. In the presence of organic carbon, SRB can reduce sulfates releasing H_2S in the process, which in turn, can result in the precipitations of insoluble secondary metal sulfides such mackinawite $[FeS]$, covellite $[CuS]$, and sphalerite $[Zn_{(1-x)}Fe_x]$. These insoluble metal sulfides are important sinks for Fe, Cu, Zn, and other dissolved metal(loid)s found in the tailings (Moncur et al., 2015).

2.5.5.4 Correlations between BACs and Geochemical Data

Significant correlations were found between BACs and the following geochemical parameters: O_2 , CO_2 , pH, Eh, alkalinity, SO_4^{2-} , and concentrations of dissolved metal(loid)s. There is a remarkable presence of iron- and sulfur-oxidizing bacteria in regions characterized by high concentrations of O_2 , Eh, SO_4^{2-} , dissolved metals (e.g., Fe, Co, Cu, Ni, Zn) and low concentrations of CO_2 and alkalinity (in Mpr20-5 and Mpr20-6), indicating that extensive sulfide-mineral oxidation processes are occurring. The abundance of iron- and sulfur-oxidizers remains elevated under acidic conditions up to a depth of approximately 1.0 mbgs. However, their abundance decreases as pH conditions increase. In Mpr20-4, iron- and sulfur-oxidizers are restricted to top 0.5 mbgs of the tailings due to minimal sulfide-mineral oxidation occurring in this location (Figure 2.14 (A)). In contrast, the quantity of S-reducing bacteria decreases with depth as the concentrations of O_2 , Eh, SO_4^{2-} , and dissolved metals decline. Additionally, as the pH values increase, the population of S-reducing bacteria also increases. Measurements for organic acids were not conducted, and the concentrations of nutrients such as nitrate were below the detection limit of ion chromatography. Therefore, no correlation analysis was performed between BACs and organic acids and nutrients.

2.5.6 Carbon Content

Solid-phase analyses indicate a low amount of total C in the oxidized tailings in both distal and proximal zones (Figure 2.18). This suggests that the amount of organic C is also low in the tailings since total C is inclusive of organic C. However, because the site is vegetated in some areas, the amount of organic C could potentially increase over time.

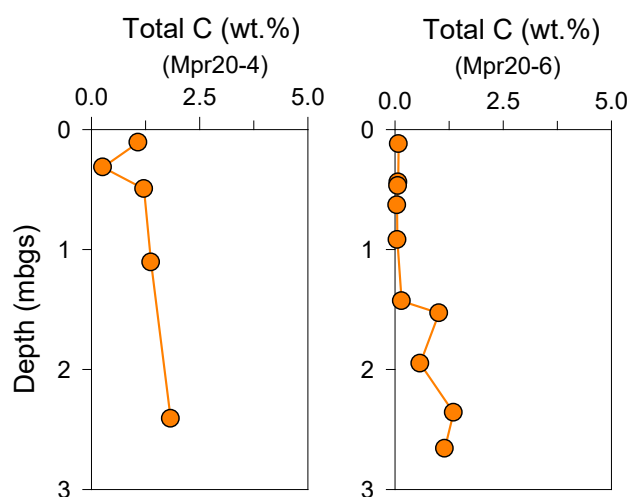


Figure 2.18. Total carbon contents of distal area (Mpr20-4) and proximal area (Mpr20-6).

2.5.7 Conclusions

Geochemical studies conducted at Parc B of Mine Principale show that sulfide minerals are heavily weathered in the area proximal to the point of tailings discharge (proximal zone) compared to the area distal to the point of tailings discharge (distal zone). Depletion of sulfide minerals and hazardous metal(loid)s such as Fe, Cu, Co, Ni, Zn, As, Pb, Cd, and Cr in the oxidized zone are indicative of the sulfide-mineral oxidation of the most prevalent sulfide minerals, pyrite, pyrrhotite, chalcopyrite, and sphalerite, along with less prevalent sulfide minerals such as pentlandite. Measurement of gas-phase O₂ and SAI are in agreement and show the extent of sulfide-mineral oxidation in the proximal zone in 2020, which is restricted to a depth of 1.5 mbgs.

Dissolved hazardous metal(loid)s show different trends in the tailings profile. Dissolved Fe, As, Pb, Cd, and Cr concentrations peak in the hardpan layer before decreasing with depth. The concentrations of dissolved Cu, Co, Ni, and Zn increase with depth, suggesting that these elements are undergoing depletion in the oxidized tailings as a result of sulfide-mineral weathering. Peaks of most metal(loid)s, in the oxidized tailings, occur at the lowest pH (2.5) of the tailings profile recorded.

Geochemical calculations indicate that the tailings profile is saturated with secondary Fe(III) (oxy)hydroxides and hydroxysulfates. This suggests that co-precipitation and adsorption with and on secondary Fe(III) (oxy)hydroxide and (oxy)hydrosulfate phases could potentially be playing a crucial role in the mobility of hazardous metal(loid)s in the tailings profile.

Synchrotron-based μ -XRF elemental mapping of weathered pyrrhotite grains show that hazardous metal(loid)s such as Ni and Co are concentrated in their alteration rims at the depths of 1.4 mbgs. Secondary Fe(III) (oxy)hydroxides and hydroxysulfates are thermodynamically stable at this depth, suggesting that elements could be incorporated into their structures via co-precipitation and/or adsorption reactions and later release to the environment via microbially mediated reduction dissolution reactions in the presence of labile organic C. While solid-phase analyses indicate a low total carbon content in the oxidized tailings, the presence of vegetation in some areas at the site suggests that it may increase in the future.

The presence of abundant S-and/or Fe-oxidizing genera indicated ongoing sulfide-mineral oxidation in the analyzed samples, primarily from Mpr20-5 and Mpr20-6. Acidophiles are more abundant than neutrophilic oxidizers due to extensive sulfide-mineral oxidation and the abundance of acidophils correlates with the bulk pH conditions. The comparison of relative abundances revealed a significantly lower abundance of sulfur and iron-oxidizing bacteria in samples from the distal zone (Mpr20-4), compared to samples from the proximal (Mpr20-5 and Mpr20-6). The bulk pH of all Mpr20-4 samples was circumneutral (while samples of pH between 2.5 and 4.2 were collected at Mpr20-5 and Mpr20-6), which likely affected the overall oxidizer populations. Also, BAC beta-diversity in Mpr20-4 samples differed from β -diversity in samples collected at Mpr20-5 and Mpr20-6 due to the difference in the extent of sulfide-mineral oxidation between them. The populations of iron-and sulfur-oxidizers exhibit a direct correlation with geochemical conditions such as O_2 , Eh, SO_4^{2-} , and concentrations of dissolved metal(loid)s in the tailings while showing an indirect correlation with geochemical parameters such as CO_2 , pH, and alkalinity. In contrast, the quantity of S-reducing bacteria decreases with depth as the concentrations of O_2 , Eh, SO_4^{2-} , and dissolved metals decline. Furthermore, as the pH values increase, the population of S-reducing bacteria also increases. No correlation was determined between BACs and nutrients and organic acids in the samples since organic acids were not measured, and concentrations of nutrients were below detection limits. No iron-reducing bacteria were found in samples, and this absence can be attributed to near atmospheric concentrations of pore gas-phase O_2 and relatively low amounts of organic matter in the oxidized zone where secondary Fe(III) (oxy)hydroxide and (oxy)hydrosulfate phases are likely to be found.

Chapter 3: Conclusions

3.1 Research Summary and Conclusions

The study at Parc B of Mine Principale focused on the potential impacts of submerging the partially oxidized tailings and adding a cover layer. The EWT technique, which involves raising the water table and maintaining it above reactive tailings, is being proposed to limit sulfide-mineral oxidation by minimizing O_2 ingress into the tailings, owing to its low diffusivity in saturated media. The application of the EWT technique, however, can cause direct dissolution of soluble secondary phases as well as inducement of reducing conditions that promote microbially mediated reductive dissolution of Fe(III) oxyhydroxide phases fueled by organic C compound and resultant release of associated hazardous metal(loid)s in the presence of labile organic C. The purpose of this study was to assess these potential impacts to help determine whether or not this proposed reclamation technique will be effective in reclaiming abandoned tailings impoundments of Mine Principale. Sampled cores used in this study were collected from Parc B. Parcs A and C were not included in this study since Starzynski (2020) had already completed a similar study using sampled cores from Parc A, and no sampled cores from Parc C were collected for analysis because of time constraint caused by COVID-19 restrictions at the time.

Parc B, where tailings are stored to an averaged depth of approximately 8.0 meters below ground surface (mbgs) has oxidized for more than 50 years as a result of exposure to atmospheric conditions. Tailings in areas proximal to the point of tailings discharge (proximal zone) are more oxidized than tailings in areas distal to the point of tailings discharge (distal zone), primarily due to two contributing factors: 1) the relatively coarse nature of the tailings, and 2) low moisture content that allow greater O_2 diffusion into the tailings. The oxidation zone in the proximal zone extended from the surface to a depth of about 1.4 mbgs, whereas distal zone tailings had mild oxidation and the oxidation zone is restricted to the depth of approximately 0.35 mbgs.

Secondary phases and associated hazardous elements found in the oxidized zone were characterized using mineralogical study (e.g., XRD, transmitted- and reflected-light optical microscopy, XRF, synchrotron based spectroscopy, etc.) and selective chemical extraction procedure. Amplicon sequencing of 16S rRNA genes was used to characterize Fe- and S-metabolizing bacteria in the tailings profile, and the amount of the total C in the oxidized tailings was approximated by solid-phase analyses.

Results from tailings pore-water indicated low pH pore-water laden with elevated concentrations of Fe, SO₄, and other dissolved metal(loid)s in the proximal zone compared to distal zone. Depletion of sulfide minerals and hazardous metal(loid)s such as Fe, Cu, Co, Ni, Zn, As, Pb, Cd, and Cr in the oxidized zone are indicative of the sulfide-mineral oxidation of the most prevalent sulfide minerals, pyrite, pyrrhotite, chalcopyrite, and sphalerite, as well as less common sulfide minerals such as pentlandite and galena. Maximum concentrations of SO₄ (12000 mg L⁻¹) and dissolved hazardous metal(loid)s (1800 mg L⁻¹ Fe, 100 mg L⁻¹ Cu, 40 mg L⁻¹ Co, 7 mg L⁻¹ Zn) were observed within the hardpan layer found in the proximal zone. Significantly altered sulfide minerals were observed in thin sections to a depth of 1.4 mbgs in the proximal zone. Mineralogical and selective chemical extraction techniques indicate the presence of various secondary phases including Fe(III) oxyhydroxides that are associated with significant amounts of hazardous metal(loid)s including Cu, Ni, Co, and Zn.

Amplicon sequencing of 16S rRNA genes show abundances of S- and Fe-oxidizing bacteria in the proximal zone and dominance of S-reducing bacteria in the distal zone at similar depths, confirming the difference in the extents of sulfide-mineral oxidation between the two zones. No correlation was determined between BACs and nutrients and organic acids in the samples since organic acids were not measured, and concentrations of nutrients were below detection limits. No iron-reducing bacteria were found in the samples, and this absence can be attributed to near atmospheric concentrations of pore gas-phase O₂ and relatively low amounts of organic matter in the oxidized zone where secondary Fe(III) (oxy)hydroxide and (oxy)hydrosulfate phases are likely to be found. The amount of organic carbon was estimated using solid-phase analyses, which indicate low amount of total C in the oxidized tailings. Organic acids measurement

was not conducted, and the concentrations of nutrients were below the detection limit of ion chromatography. Therefore, no correlation analysis was performed between BACs and organic acids and nutrients.

Given the overall limited extent of sulfide-mineral oxidation (about 1.5 mbgs in the most oxidized zone of Parc B), low amount of organic carbon, absence of Fe-reducing bacteria, great abundance of desulfurized tailings (from Parc C), and presence of S-reducing bacteria that may promote formation of sparingly insoluble sulfides from dissolved hazardous metal(loid)s including Fe, Cu, and Zn, the EWT technique can be an effective reclamation method for Mine Principale tailings if use in conjunction with another appropriate method to treat any significant contaminated effluent that may be generated as a result of water saturation and redox conditions that may promote solubilisation of secondary minerals in the oxidized zone following the application of EWT.

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Appendices

A. Solid Geochemistry

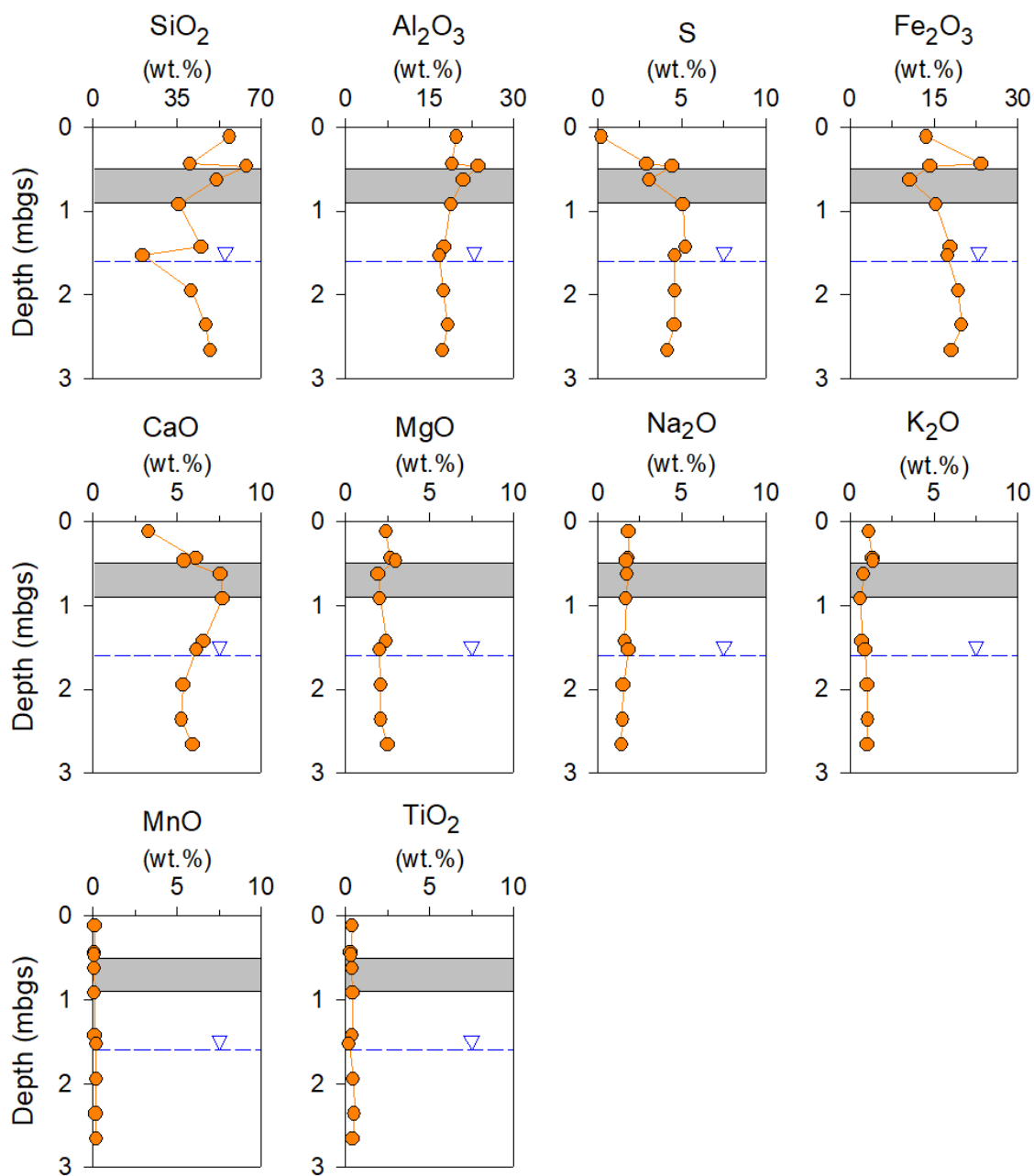


Figure 0.1. Powder XRF data on major oxides/elements from Mpr20-6 (2020). Water table depth was estimated on collection of water in the cored holes.

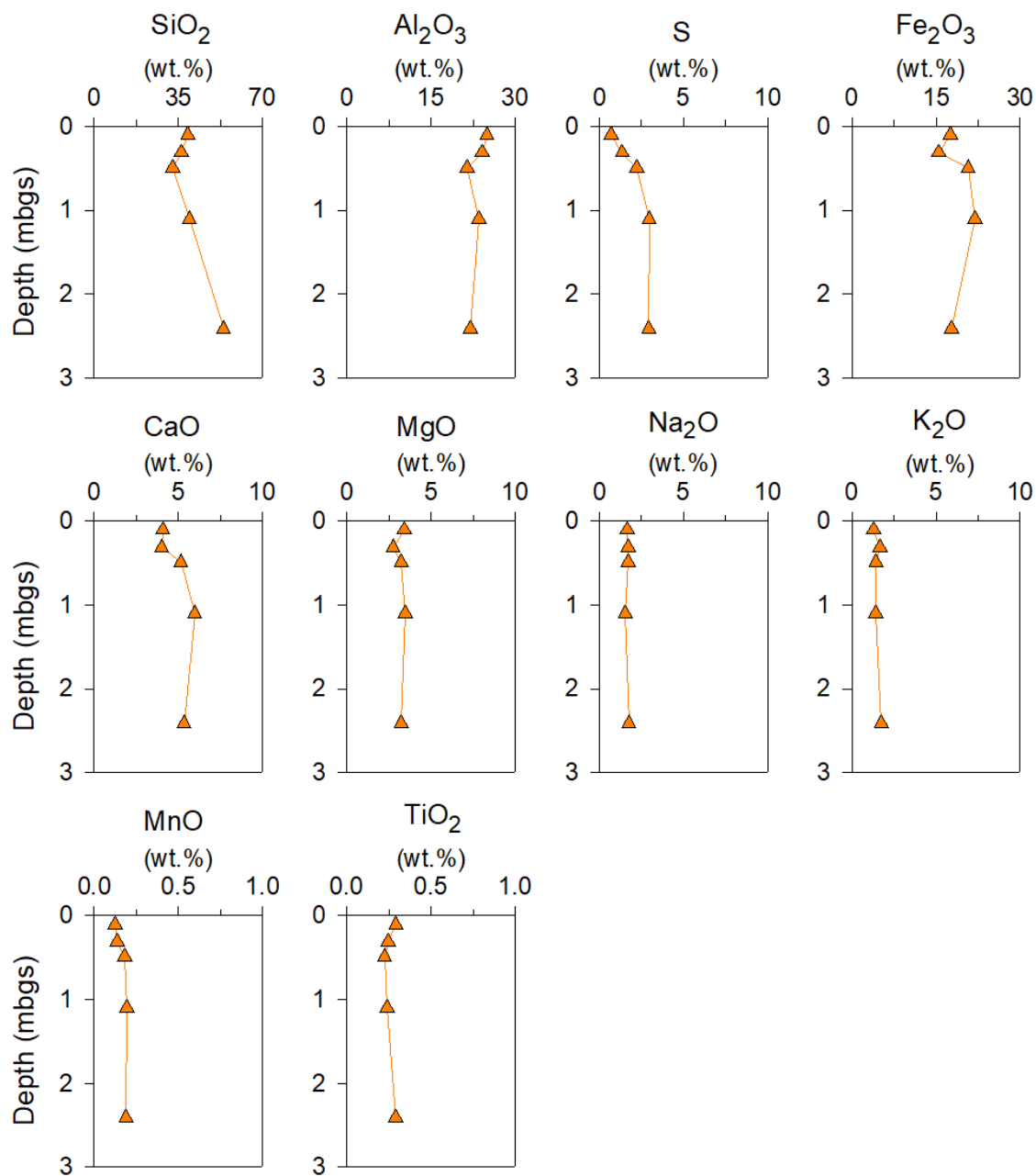


Figure 0.2. Powder XRF data on major oxides/elements from Mpr20-4 (2020).

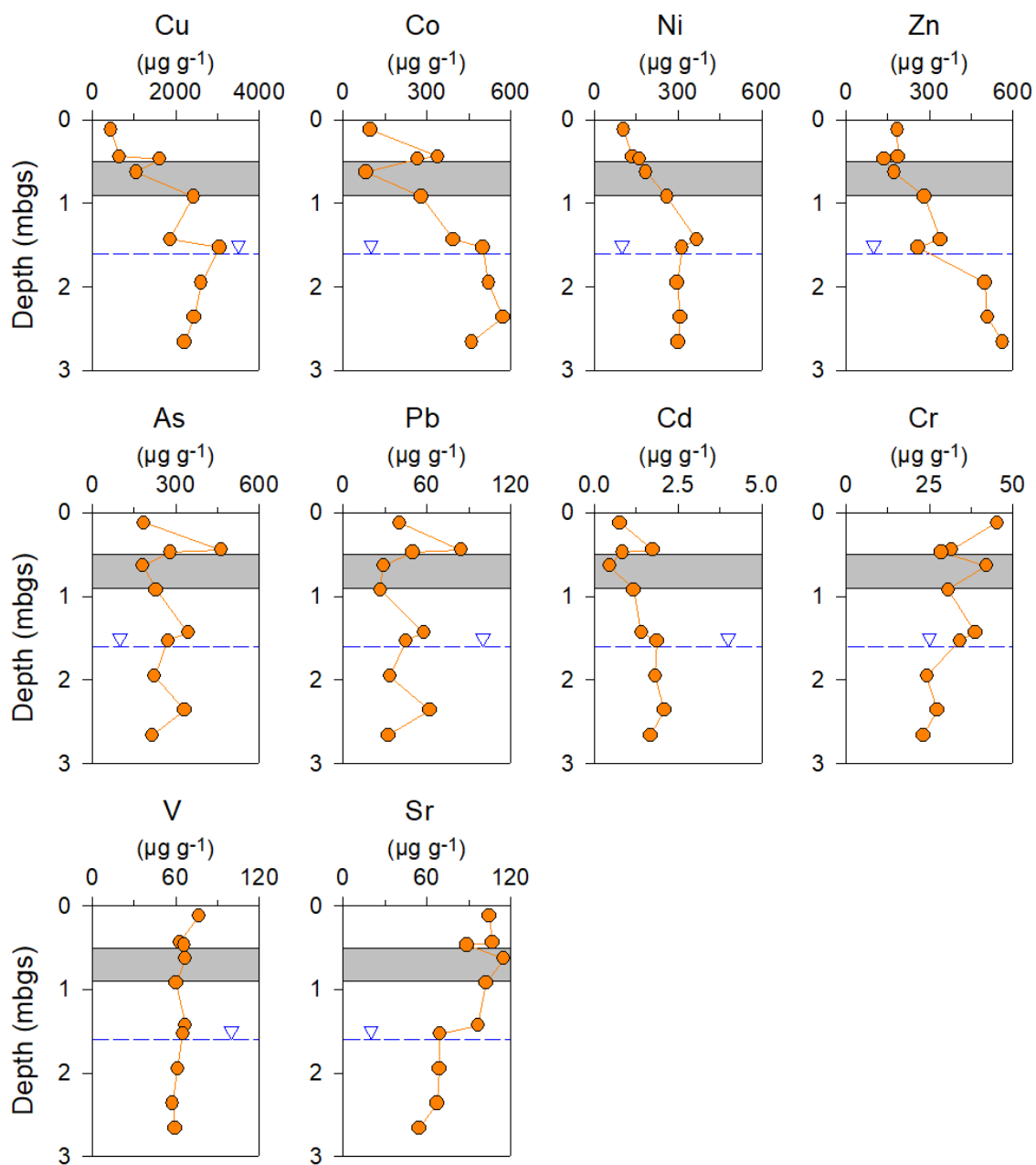


Figure 0.3. Powder XRF data on trace metal(loid)s from Mpr20-6 (2020). Water table depth was estimated on collection of water in the cored holes.

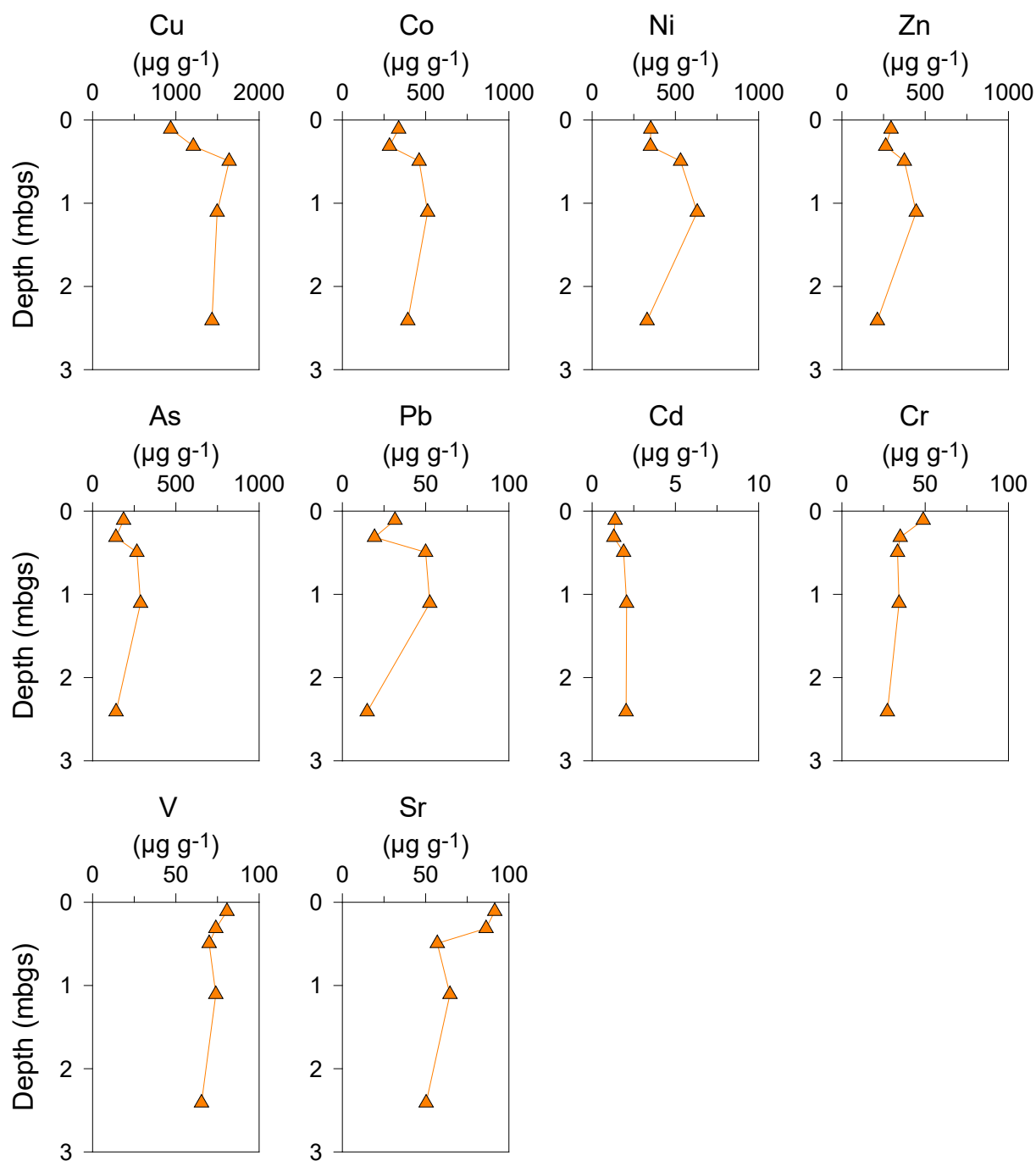


Figure 0.4. Powder XRF data on trace metal(loid)s from Mpr20-4 (2020).

B. Aqueous Geochemistry

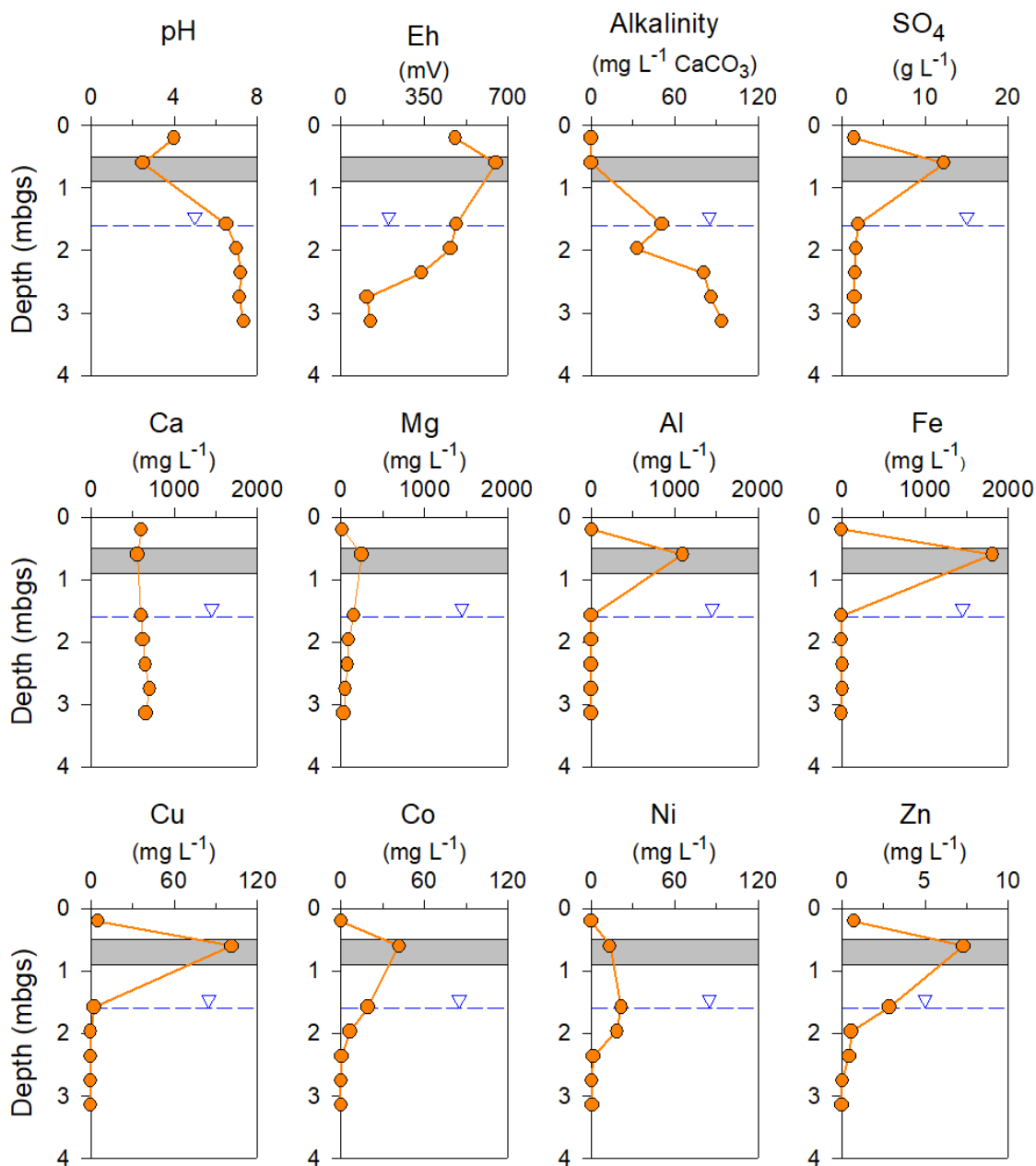


Figure 0.5. Geochemistry of the pore-water at Mpr20-6 from core squeezing (2020). Water table depth was estimated on collection of water in the cored holes.

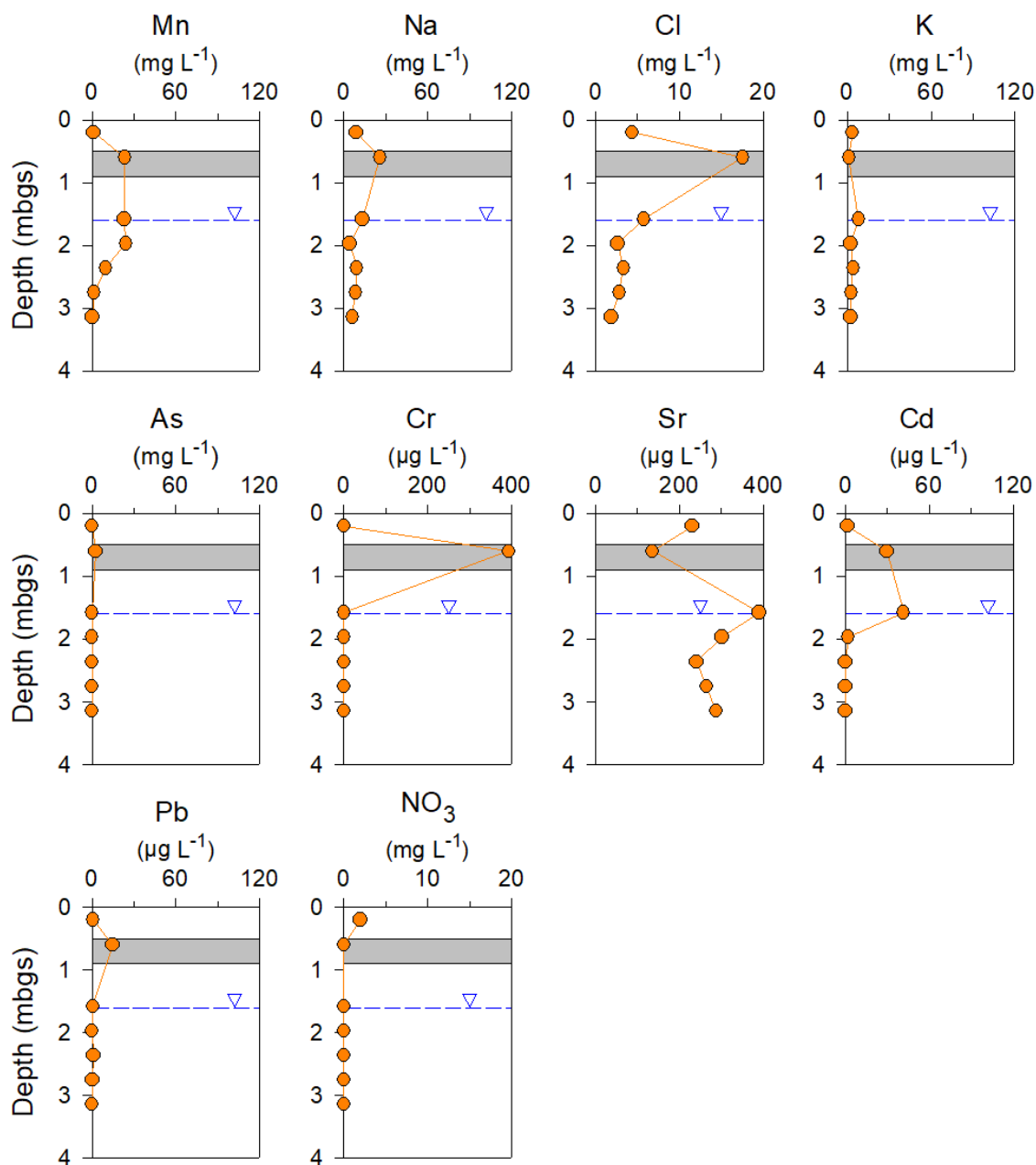


Figure 0.6. Geochemistry of the pore-water at Mpr20-6 from core squeezing (2020). Water table depth was estimated on collection of water in the cored holes.

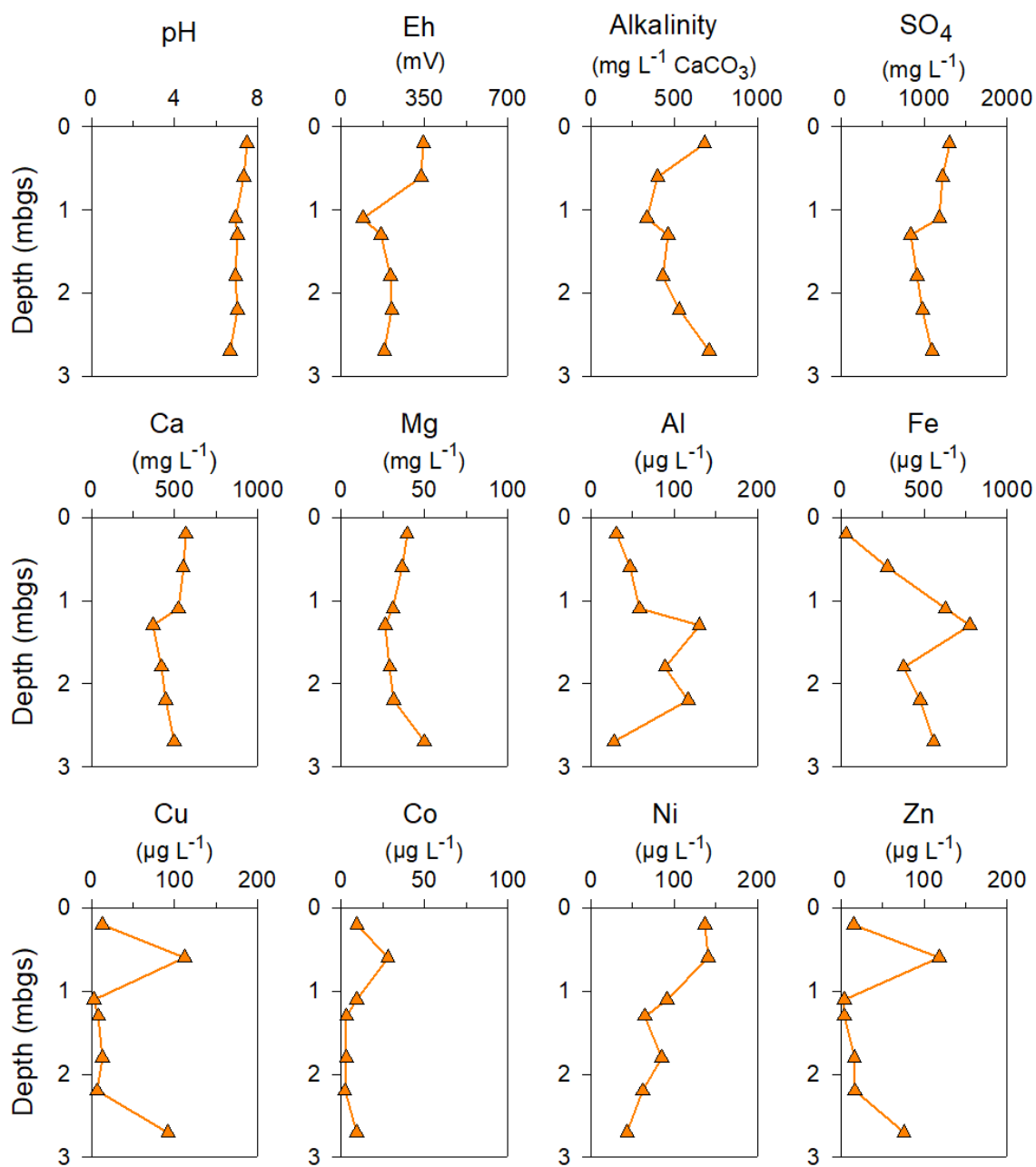


Figure 0.7. Geochemistry of the pore-water at Mpr20-4 from core squeezing (2020).

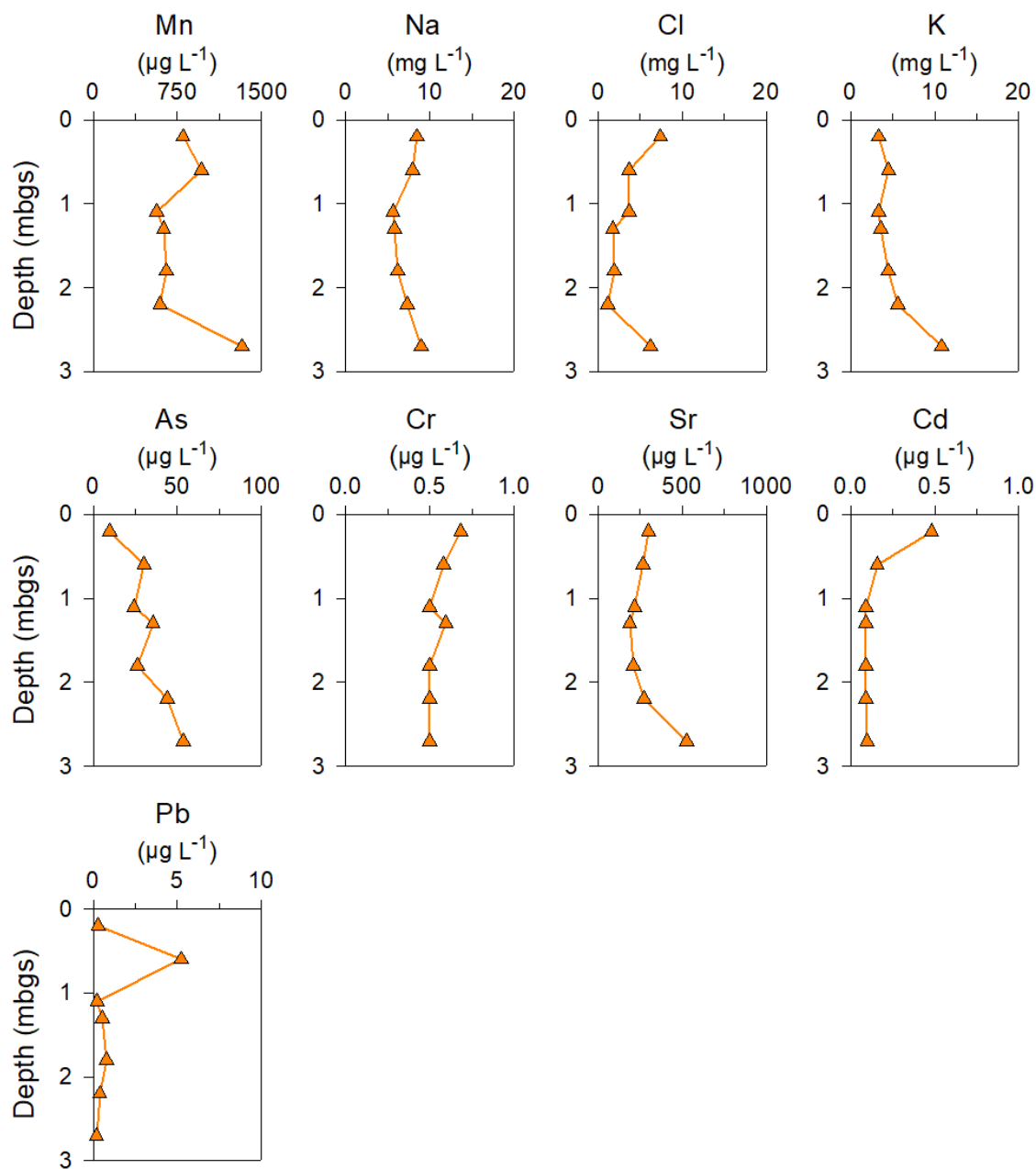


Figure 0.8. Geochemistry of the pore-water at Mpr20-4 from core squeezing (2020).

C. Chemical Extractions

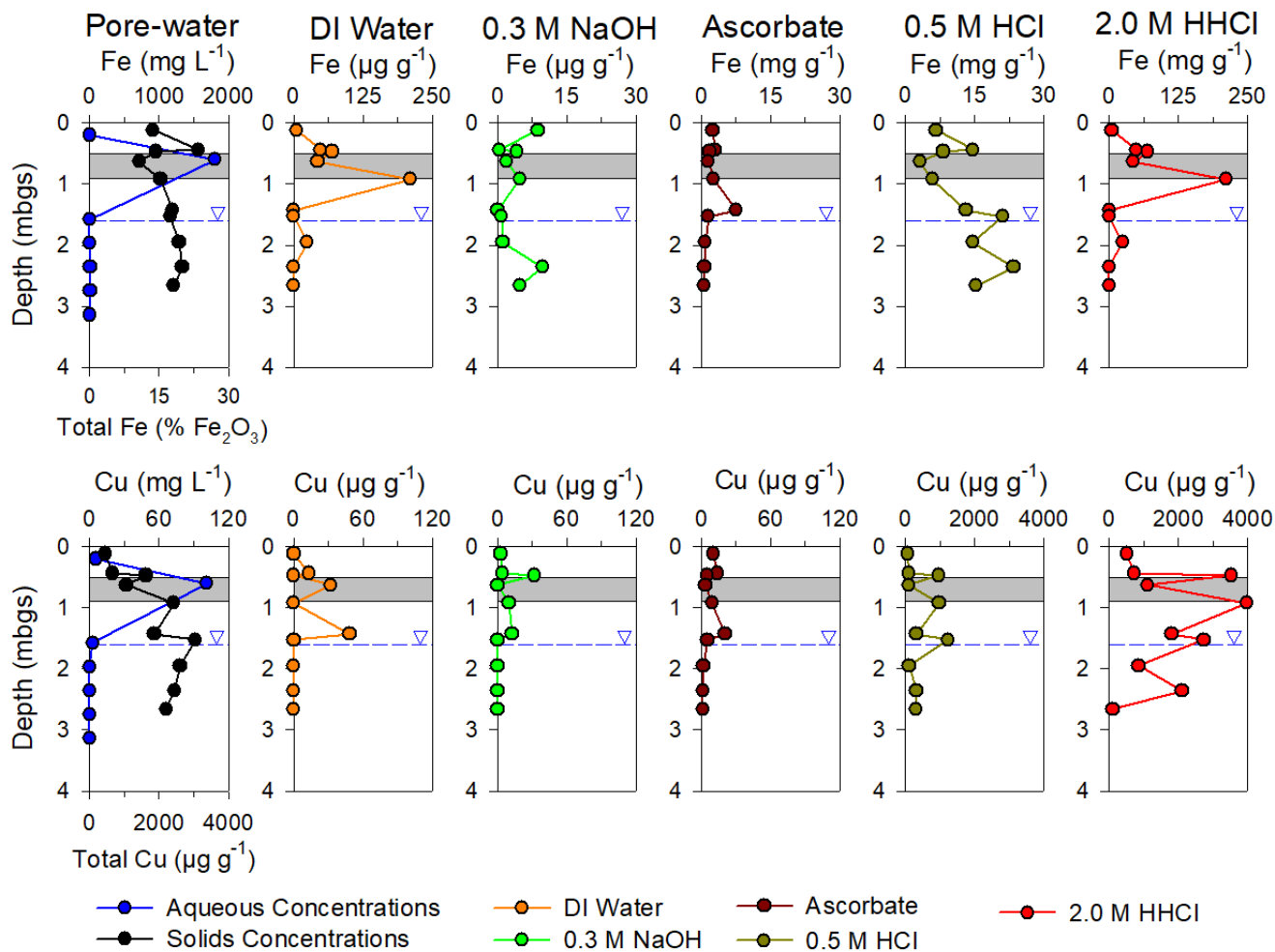


Figure 0.9. Results from selective extractions plotted against depth and geochemical profiles of Fe and Cu for Mpr20-6 (2020). The shaded grey area represents the hardpan and the dashed line with inverted triangle indicates the water table. Water table depth was estimated on collection of water in the cored holes.

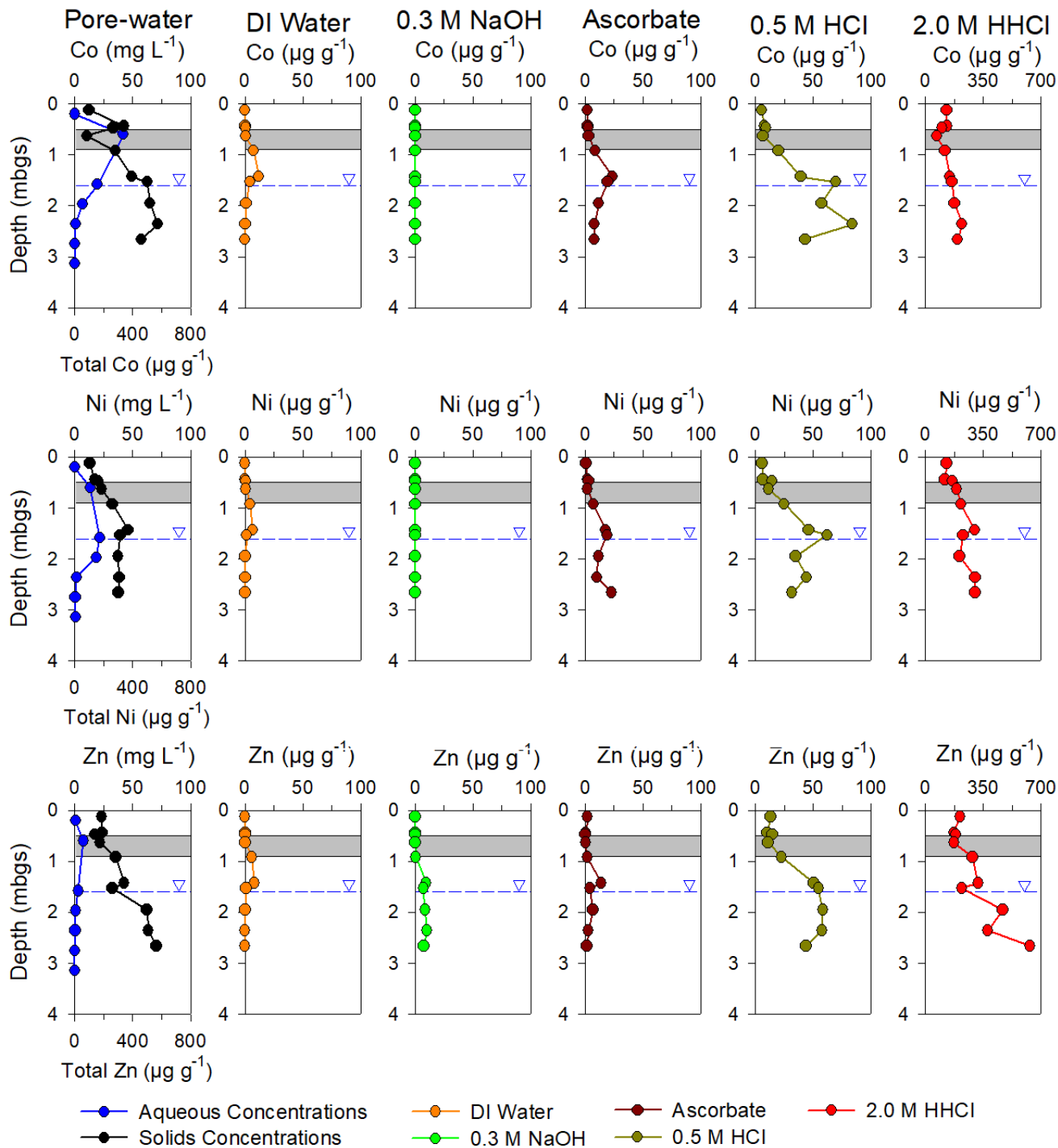


Figure 0.10. Results from selective extractions plotted against depth and geochemical profiles of Co, Ni, and Zn for Mpr20-6 (2020). The shaded grey area represents the hardpan and the dashed line with inverted triangle indicates the water table. Water table depth was estimated on collection of water in the cored holes.

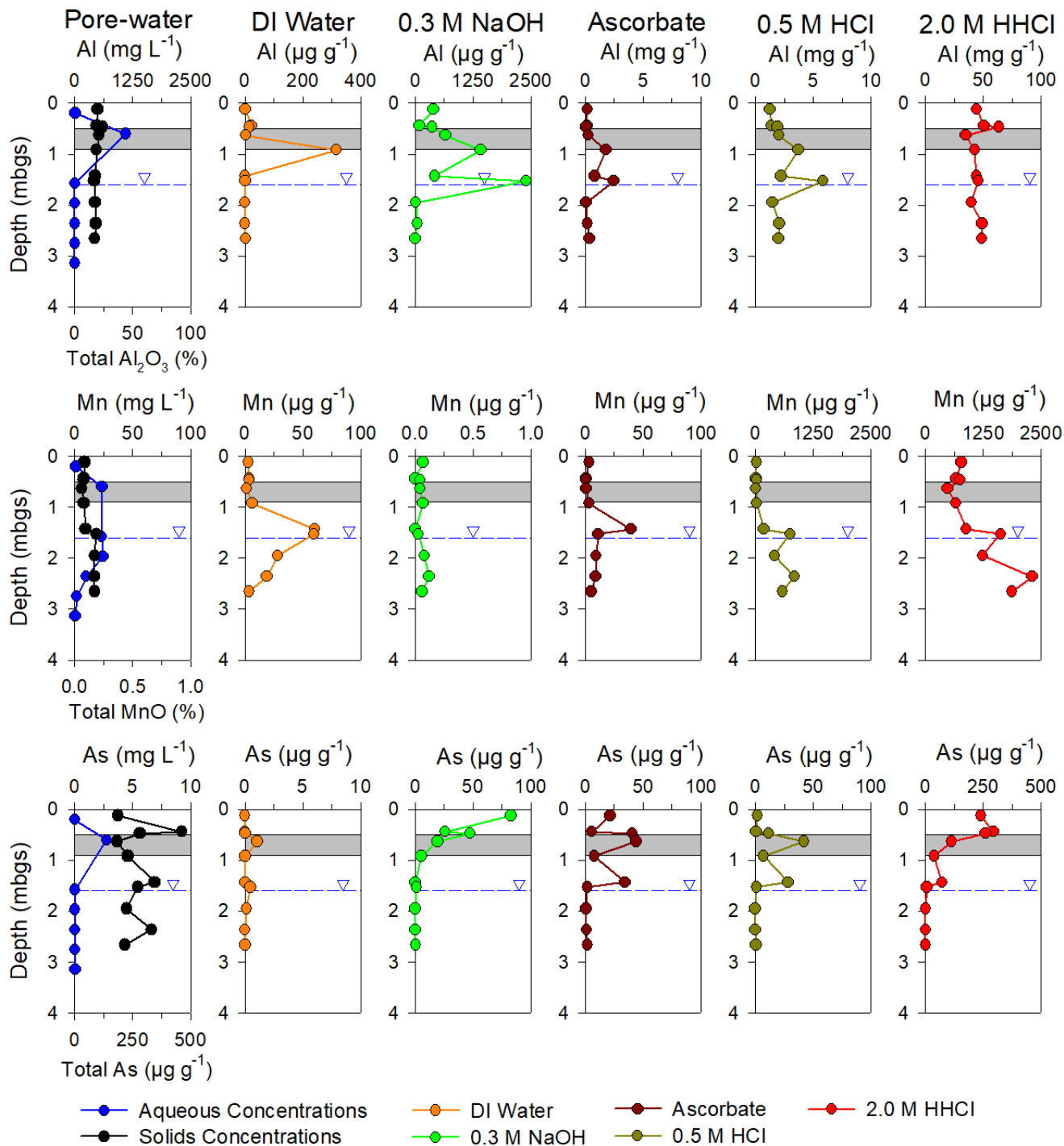


Figure 0.11. Results from selective extractions plotted against depth and geochemical profiles of Al, Mn, and As for Mpr20-6. The shaded grey area represents the hardpan and the dashed line with inverted triangle indicates the water table. Water table depth was estimated on collection of water in the cored holes.

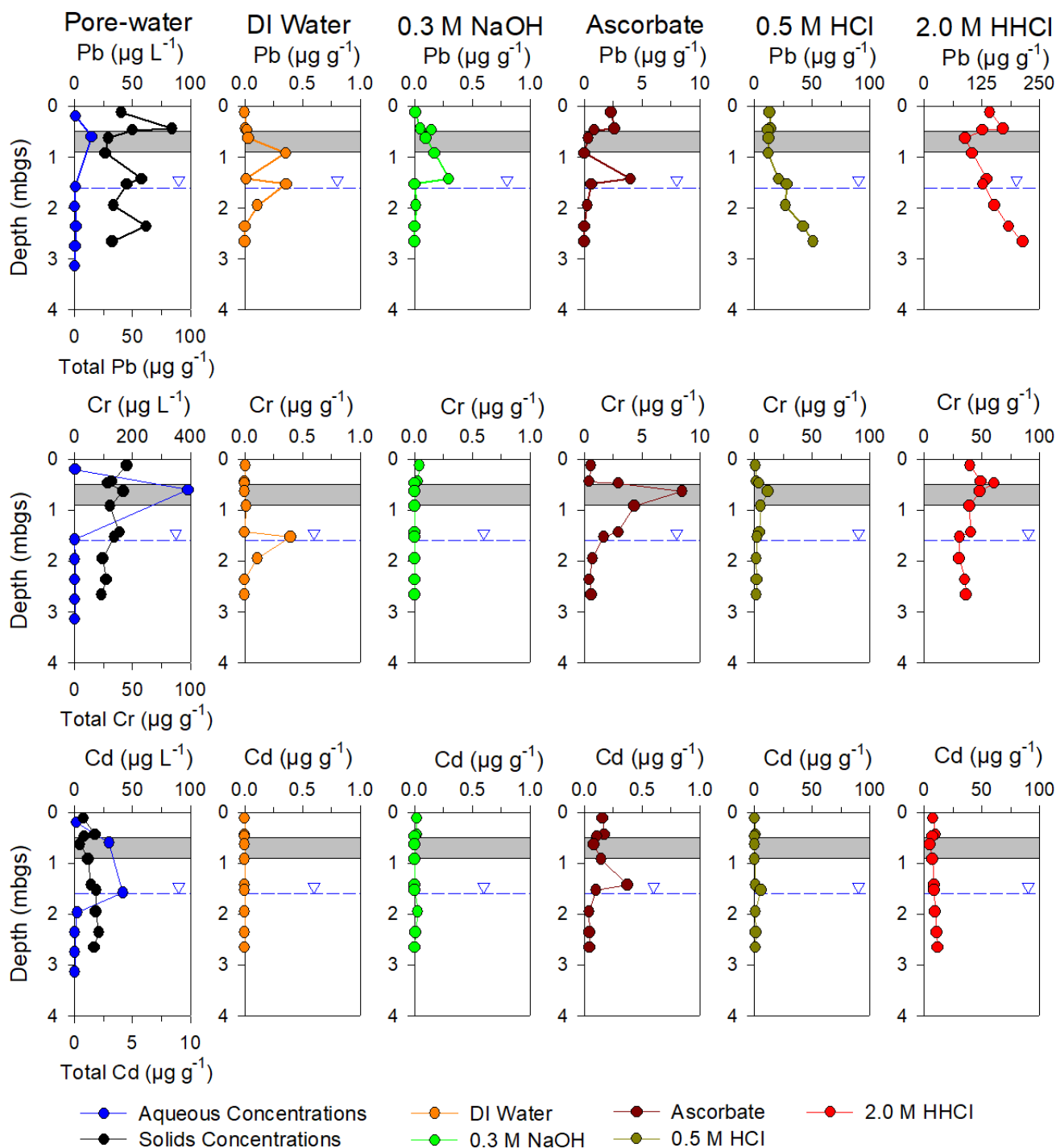


Figure 0.12. Results from selective extractions plotted against depth and geochemical profiles of Pb, Cr, and Cd for Mpr20-6. The shaded grey area represents the hardpan and the dashed line with inverted triangle indicates the water table. Water table depth was estimated on collection of water in the cored holes.

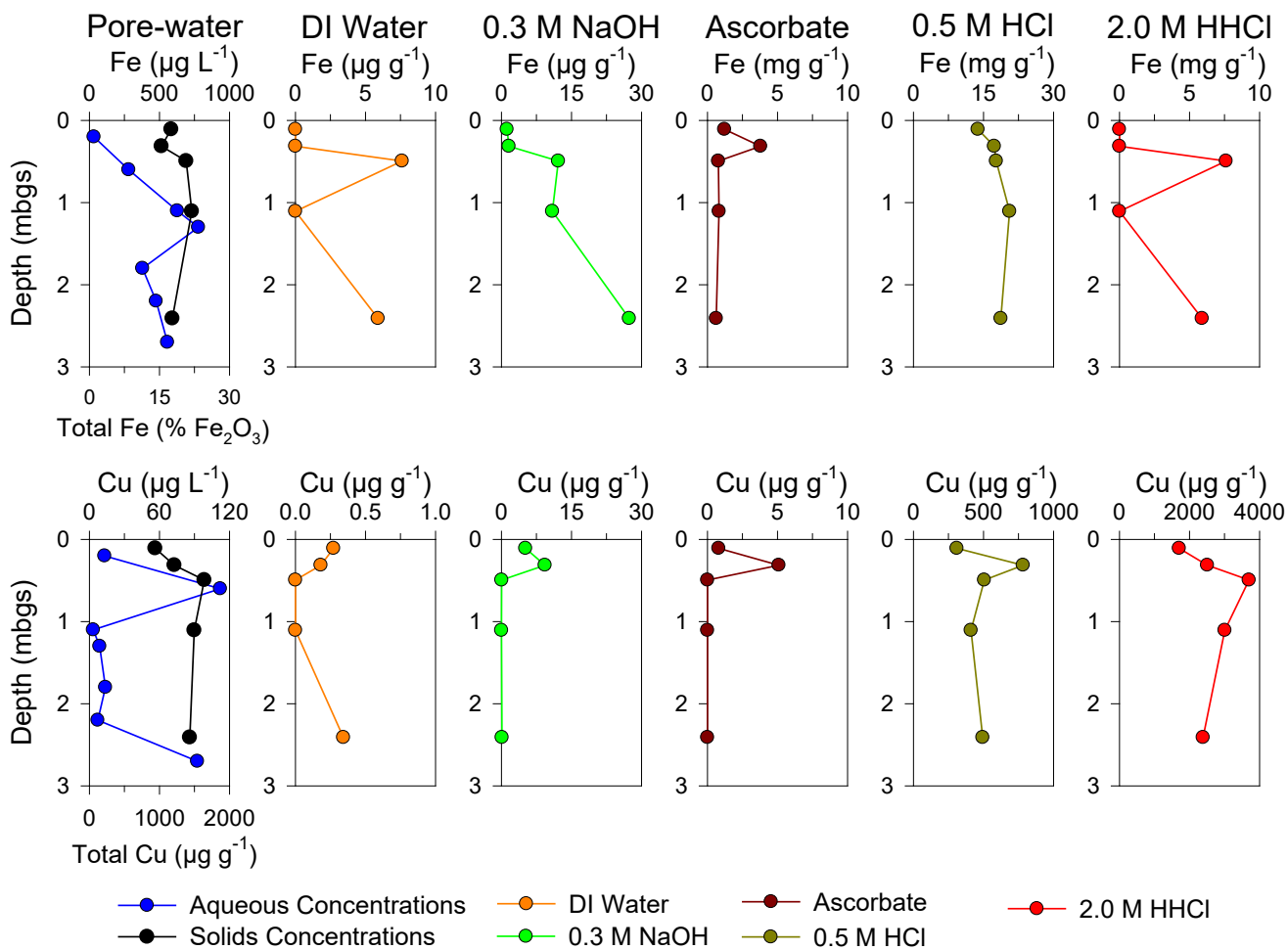


Figure 0.13. Results from selective extractions plotted against depth and geochemical profiles of Fe and Cu for Mpr20-4.

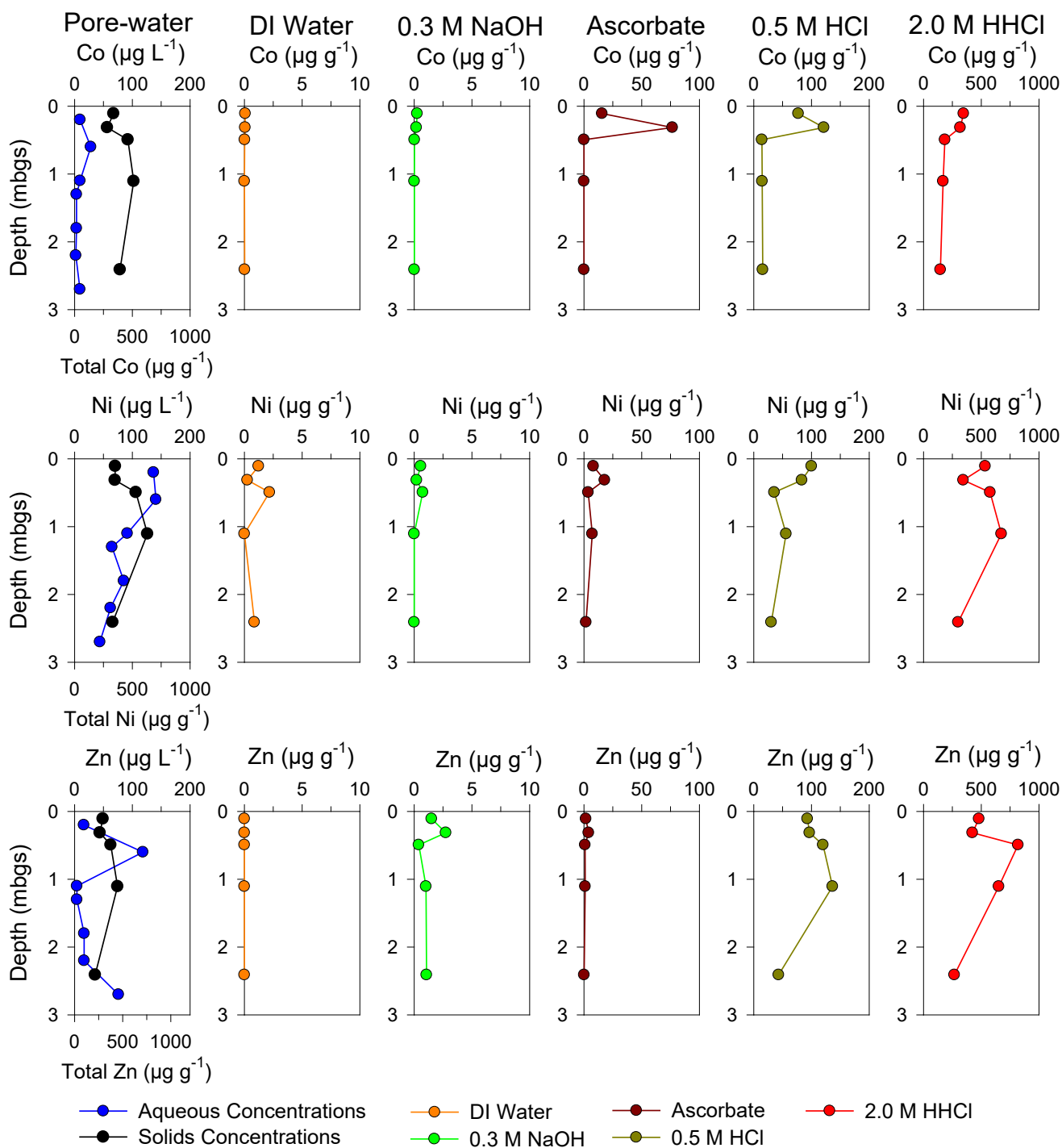


Figure 0.14. Results from selective extractions plotted against depth and geochemical profiles of Co, Ni, and Zn for Mpr20-4.

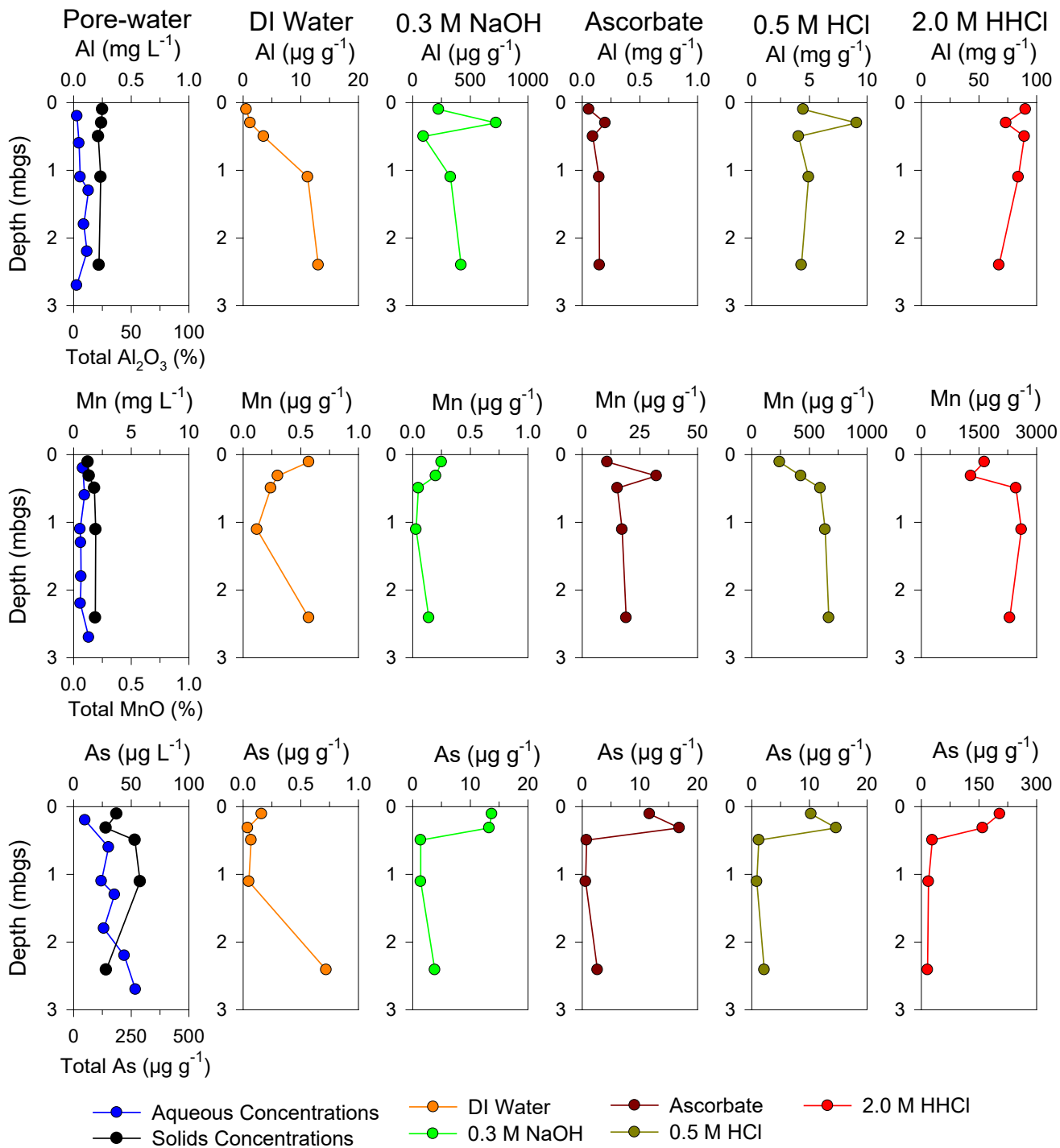


Figure 0.15. Results from selective extractions plotted against depth and geochemical profiles of Al, Mn, and As for Mpr20-4.

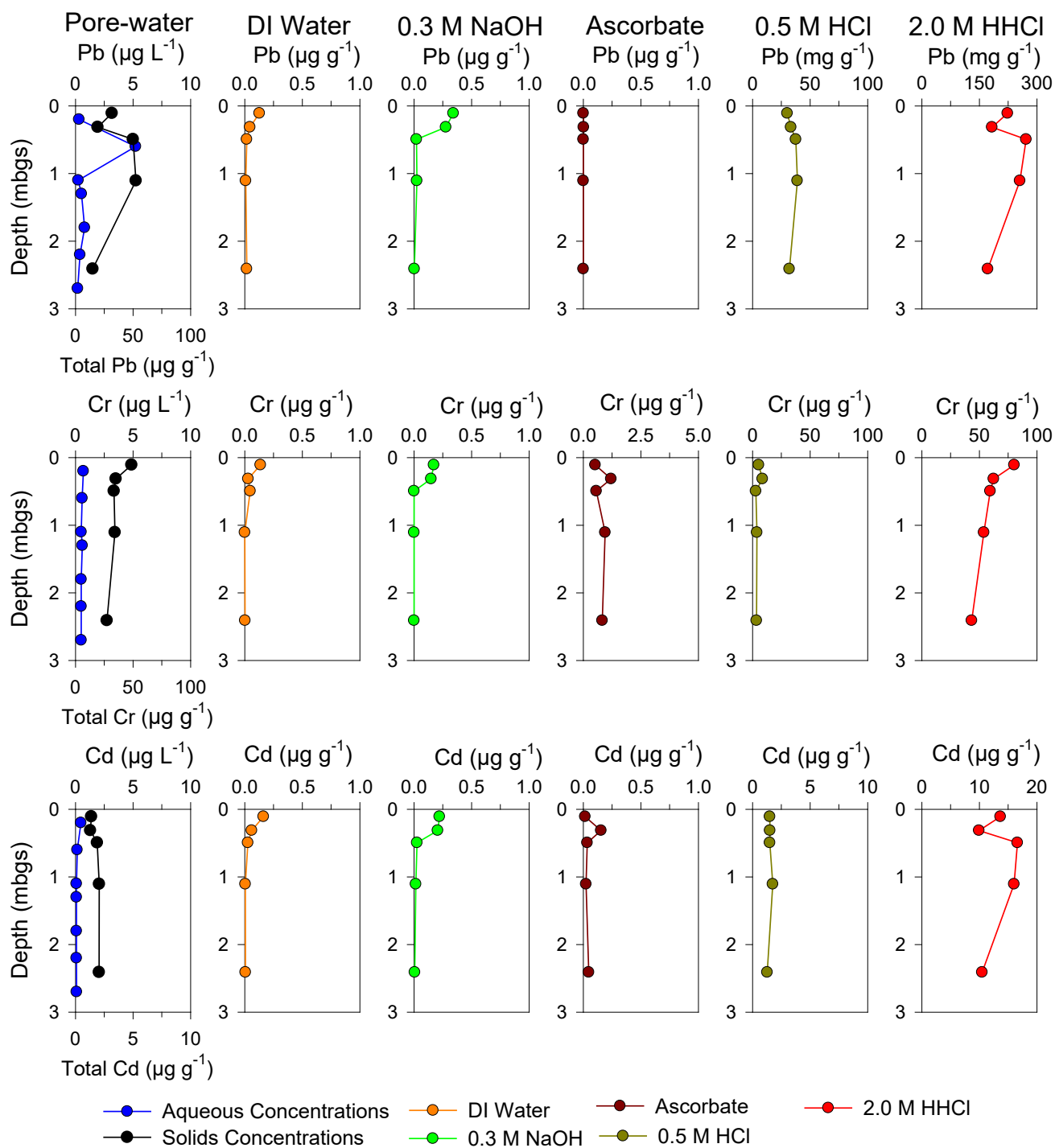


Figure 0.16. Results from selective extractions plotted against depth and geochemical profiles of Pb, Cr, and Cd for Mpr20-4.

Table 0.1. Total numbers of raw and effective sequences, OTU (operational taxonomic unit) counts, and alpha-diversity indices (Good's coverage, Chao's, and Gini-Simpson's indexes). Legend: Triplicate samples are marked with asterisk.

Site	Depth (m)	Total raw sequences	Effective sequences for analysis	OTU counts	Good's coverage	Chao's index	Gini-Simpson's index
Mpr20-4	0.11	33448	30390	261	0.992	252	0.813
	0.32	13908	12915	136	0.996	135	0.895
	0.50	9949	9399	46	0.997	69	0.312
	1.11	30343	28512	87	0.997	227	0.300
	2.41	30039	27745	389	0.992	345	0.975
Mpr20-5	0.02	62370	55002	578	0.996	424	0.913
	0.30	31672	28517	231	0.995	215	0.839
	0.44	52500	48454	181	0.997	117	0.863
	0.46	47206	44095	124	0.994	99	0.195
	0.53	21669	19994	84	0.994	86	0.616
	0.82*	61192	56757	215	0.998	144	0.412
	0.82*	64450	59465	275	0.984	176	0.819
	0.82*	8490	7843	76	0.992	80	0.821
	1.07	75910	69727	290	0.994	171	0.773
	1.71	29277	26881	312	0.993	286	0.950
	2.41	17981	15802	145	0.997	151	0.928
Mpr20-6	0.12	34455	30943	351	0.992	312	0.957
	0.44	15335	13618	153	0.995	158	0.914
	0.47	7323	6360	101	0.996	110	0.574
	0.63	46248	41301	154	0.995	132	0.833
	0.92	49580	44346	201	0.995	146	0.856
	1.43	11712	11043	79	0.996	100	0.824
	1.53	30246	27891	209	0.994	189	0.946
	1.95	30872	27536	181	0.996	168	0.842

Table 0.2. Mean proportions of total reads of major bacterial genera (mean relative abundance > 0.5% of total amplicons) and sum of minor genera (< 0.5%). Higher taxa that could not be identified on the genus level are marked with asterisks.

Genus	%
Sum of minor genera	52.75
<i>Bacteria</i> *	8.98
<i>WPS-2_ge</i>	7.33
<i>Proteobacteria</i>	2.62
<i>Gammaproteobacteria</i>	2.51
<i>Pseudomonas</i>	1.68
<i>Acidiferrobacteraceae</i>	1.23
<i>Desulfosporosinus</i>	1.16
<i>Candidatus_Woesebacteria_ge</i>	1.05
uncultured	1.05
<i>Sva0485_ge</i>	1.01
<i>B12-WMSP1_ge</i>	0.90
<i>Acidithiobacillus</i>	0.90
<i>Coxiella</i>	0.90
uncultured_ge	0.86
<i>BSV13</i>	0.86
<i>Babeliales</i> *	0.86
<i>Acidimicrobiia</i> *	0.82
<i>Ruminococcaceae</i> *	0.79
uncultured_ge	0.75
<i>Legionella</i>	0.75
<i>Actinobacteria</i> *	0.71
<i>Acidibacillus</i>	0.71
<i>Acetobacteraceae</i> *	0.71
<i>Burkholderiaceae</i> *	0.71
uncultured	0.67
<i>Betaproteobacteriales</i> *	0.67
uncultured	0.64
<i>Subgroup_6_ge</i>	0.64
<i>IMCC26256_ge</i>	0.64
uncultured_ge	0.64
<i>Leptospirillum</i>	0.64
<i>Aquicella</i>	0.64
<i>Thiobacillus</i>	0.60
<i>Candidatus_Shapirobacteria_ge</i>	0.56
<i>Xanthomonadales</i> *	0.56
<i>Clostridia</i>	0.52

Table 0.3. Mean proportions of total reads of sulfur- and/or iron-metabolizing genera. Higher taxa that could not be identified on the genus level are marked with asterisks. Legend: SRB=sulfate-reducing bacteria, SOM/IOM=sulfur- and iron-oxidizers, SOM=sulfur-oxidizers.

Genus	% of total reads
SRB:	
<i>Desulfosporosinus</i>	1.16
<i>Desulfurispora</i>	0.37
<i>Desulfobulbaceae*</i>	0.22
<i>Desulfotobacterium</i>	0.19
<i>Desulfocapsa</i>	0.19
<i>Candidatus_Desulforudis</i>	0.11
<i>Desulfobacca</i>	0.11
<i>Desulfatiglans</i>	0.07
<i>Desulfatirhabdium</i>	0.07
<i>Desulfotomaculum</i>	0.04
<i>Desulfobacteraceae*</i>	0.04
<i>Desulfobulbaceae_ge</i>	0.04
<i>Desulfurivibrio</i>	0.04
<i>Desulfuromonas</i>	0.04
<i>Desulfomonile</i>	0.04
<i>Shewanella</i>	0.04
SOM/IOM:	
<i>Acidiferrobacteraceae*</i>	1.23
<i>Acidithiobacillus</i>	0.90
<i>Acidibacillus</i>	0.71
<i>Acidiferrobacter</i>	0.49
<i>Sulfobacillus</i>	0.41
<i>Alicyclobacillus</i>	0.19
<i>Alicyclobacillaceae*</i>	0.04
IOM:	
<i>Acidimicrobium*</i>	0.82
<i>Leptospirillum</i>	0.64
<i>Gallionellaceae*</i>	0.22
<i>Ferrithrix</i>	0.15
<i>Acidithrix</i>	0.04
<i>Ferrimicrobium</i>	0.04
<i>Gallionella</i>	0.04
SOM:	
<i>Thiobacillus</i>	0.60
<i>Sulfurifustis</i>	0.22
<i>Sulfuriferula</i>	0.22
<i>Acidiphilium</i>	0.15
<i>Sulfurovum</i>	0.11
<i>Ferrovum</i>	0.11

<i>Sulfuricella</i>	0.11
<i>Acidicaldus</i>	0.04
<i>Sulfuritalea</i>	0.04
<u><i>Sulfurirhabdus</i></u>	0.04

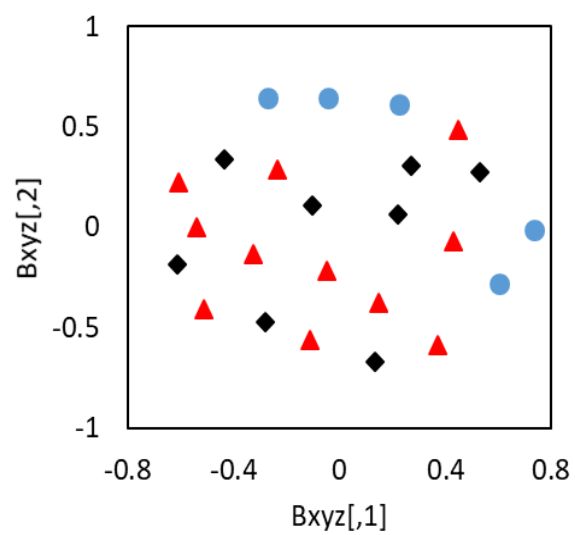


Figure 0.17. 2D-NMDS plot (stress=0.379) of unweighted UniFrac used to investigate BACs in (●) Mpr20-4, (▲) Mpr20-5, and (◆) Mpr20-6 samples. The distance between any two points represents the difference between those two communities.