

**EFFECTS OF WEATHERING ON CHEMICAL AND MINERALOGICAL
PROPERTIES OF THE MOUNT POLLEY MINE TAILINGS: PRELIMINARY
IMPLICATIONS FOR LONG-TERM ECOSYSTEM HEALTH**

by

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Abstract

The Mount Polley Mine's tailings storage facility failure deposited large amounts of relatively unweathered material of a range of mineralogical and chemical composition over the Hazeltine Creek channel in Secwepemc territory. Reclamation efforts focus on the present chemical composition and sequential extractability of metals in the tailings. This precursory research focuses on the surface reactions of the tailings material and the effect that acids have on altering surface chemistry of these fresh tailings deposits in relation to environmental risk standards. Through laboratory simulation experiments, acid ammonium oxalate, hydrochloric acid, and *aqua regia* treatments, tailings composition under simulated acid weathered conditions were examined. The deposited tailings are characterized by low aeration and porosity, alkaline pH and very limited organic matter. Cu and V were readily available in concentrations that exceed the CSR regulations for the protection of soil invertebrates and plants. Exploratory PCA analysis suggested that the chemical composition of the tailings is not depth dependent, but spatial and material segregations were evident. XRD diagrams of tailings under simulated weathering conditions illustrate that the material has variable susceptibility to weathering. Calcite, magnetite and chlorite group minerals were removed by acid ammonium oxalate and hydrochloric acid treatments, while the more stable feldspar group minerals (albite, microcline), muscovite and quartz persisted despite treatment with the strong acid, *aqua regia*. Apatite group minerals were found in the majority of the raw samples. Elemental analysis revealed high concentrations of extractable P in the tailings. Longer-term monitoring of the receiving aquatic environments is recommended. Removal of tailings from the Hazeltine Creek channel is encouraged as is combining remnant tailings with organic material and till to improve aeration, porosity and structure, promote metal complexation and provide N for re-vegetation.

Lay Summary

The Mount Polley Mine tailings storage facility failure of 2014 was one of the industry's most dramatic incidents that has happened in Canada. There have been a growing number of concerns raised by community members, organizations, academics and government officials regarding the ecological, human health and spiritual impact of this event. At the time of sampling in 2016 a large proportion of the tailings remained where it was deposited along the Hazeltine Creek channel. As it interacts with the surface conditions of the natural riparian environment, the material begins to undergo chemical alterations. This exploratory research sets the stage for the longer-term dynamics of tailings weathering and the release of potentially toxic elements.

Preface

This dissertation is original, unpublished work by the author, Elana Evans. It is composed of 4 body chapters that were supervised by Dr. Les Lavkulich. I collected the Mount Polley Mine tailings samples with the assistance of Dixi Modi in June of 2016. XRD analysis was done with the assistance of Lan Kato, and Elisabetta Pani from the Department of Earth, Atmospheric and Ocean Sciences (EAOS). Maureen Soon, also from EAOS, assisted with ICP-OES. Statistical analysis was done with the help of Dr. Gary Bradfield.

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List of Symbols

Al	Aluminum
A _e	A soil mineral surface layer that is characterized by the eluviation of clay, Fe, Al, or organic matter alone or in combination.
As	Arsenic
B _f	A soil mineral layer enriched in Al and Fe, commonly found in podzolic soils
B _t	A soil mineral layer that is characterized by having illuvial layer lattice clays
C	Carbon
Ca	Calcium
CaCl ₂	Calcium Chloride
Cd	Cadmium
Cl	Chlorine
cm	Centimeters
Co	Cobalt
CoK α	Cobalt, the XRD target element for characteristic wave length α for XRD
CO ₂	Carbon Dioxide
CO ₃	Carbonate
Cr	Chromium
Cu	Copper
CuFeS ₂	Chalcopyrite
Cu ₅ FeS ₄	Bornite
CuS	Covellite
Cu ₉ S ₅	Digenite
Fe	Iron
FeS ₂	Pyrite
g	Grams
H ⁺	Hydrogen ions
H ₂ CO ₃	Carbonic Acid
HCO ₃ ⁻	Bicarbonate
HCl	Hydrochloric Acid

H ₂ O	Water
Hg	Mercury
HF	Hydrofluoric Acid
HNO ₃	Nitric Acid
IAP	Ion-activity Product
K _{sp}	Solubility Product
Km	Kilometer
Kg	Kilogram
LFH	A soil organic surface layer containing >17% organic C that is typically associated with upland forest soils
m	Meters
mL	milliliters
Mn	Manganese
Mg	Magnesium
Mo	Molybdenum
Na	Sodium
Ni	Nickle
O ₂	Oxygen
P	Phosphorus
ppm	Parts per million
Pb	Lead
S	Sulfur
Se	Selenium
Si	Silica
SI	Saturation Index
V	Vanadium
Zn	Zink
°C	Degree Celsius

List of Abbreviations

ARD	Acid Rock Drainage
AAO	Acid Ammonium Oxalate
BC	British Columbia
BD	Bulk Density
EPA	Environmental Protection Agency
COPC	Contaminants of Potential Concern
CSR	Contaminated Sites Regulation
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometer
M	Mean
PCA	Principal Component Analysis
PD	Particle Density
SE	Standard Error
Std Dev	Standard Deviation
SOM	Soil Organic Matter
TSF	Tailings Storage Facility
XRD	X-Ray Diffraction

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I love you always, Baba.

Chapter 1: Introduction

1.1 Study Overview

In the summer of 2014, the tailings storage facility (TSF) at the Mount Polley copper and gold mine breached and approximately 25 million cubic meters of tailings slurry flowed out of the impoundment and into the surrounding forest, riparian and aquatic ecosystems. As a result, over 200 hectares of land were either covered with a layer of deposited tailings or scoured by it. Major ecosystem health concerns are associated with the release of metals, acid effluents and contaminants from tailings at mine sites (WISE Uranium Project, 2017). The importance of measuring metals in the tailings material along the banks of Hazeltine Creek in order to evaluate its contamination potential and toxicity, is an essential first step in order to make comparison statements over a period of time. Because not all metals are equally available and/or mobile, characterizing the elemental associations within mineralogical structures is necessary in order to understand the potential ecosystem health risks of the tailings storage facility failure.

The tailings released during the TSF spill were fresh, relatively un-weathered geologic material. When exposed to oxidizing environments at earth's surface temperatures and pressures, the minerals undergo chemical alterations. Many of the weathering reactions and chemical changes occur at the surface level of mineral fractions over geologic, or pedological, time-scales and therefore, the ability to observe and measure them in the field over different periods of time, first requires careful analysis of the fresh or un-weathered tailings. Thus, this preliminary information is important because the tailings are known to contain elevated concentrations of potentially toxic elements whose release by weathering and subsequent mobility may pose environmental and human health hazards.

This exploratory study examined the surface properties of the Mount Polley tailings materials and the effects that acidic weathering agents have on the availability, mobility and retention behaviour of Al, Ca, Fe, Mn, Mg, Cu, Na, P, Zn, Pb, Cr, Co, Ni, Mo, Cd, V, Se. All elements were considered in relation to environmental risk standards proposed by the Canadian Soil Quality Guideline for the Protection of Environmental and Human Health and the BC Contaminated Sites Regulation. Weathering processes were simulated in the laboratory with three different acids. Hydrochloric acid was used to evaluate the effects that low pH had on elemental

mobility, acid ammonium oxalate was used for its strong chelating properties to assess metal bioavailability and *aqua regia* was used to determine total recoverable elements in the tailings. All elemental analysis was performed using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). X-Ray Diffraction (XRD) was used to determine mineral composition before and after acid treatments.

A rigorous restoration effort is underway at the Mount Polley mine spill site; notable amounts of the tailings have been removed from the Hazeltine Creek channel. This study contributes insights into the mobility and bioavailability of elements that are enriched in the tailings and the changes that are likely to occur at the mineralogical level. Short term clean-up is essential but limited, unless restoration work responds to more long-term risks of slow metal release.

1.2 Site Description

The Mount Polley Mine is located in the northern reaches of the traditional and un-ceded territories of the Secwepemc people. Three First Nations communities suffered direct, immediate and ongoing impacts from the Tailings Storage Facility failure in 2014. They are the Xat'sull (Soda Creek Indian Band), T'exelcenc (Williams Lake Indian Band) and Lhatko Dene First Nation communities (Shandro et al, 2016). The mine site is situated in the Quesnel River Basin watershed about 57 kilometers northeast of Williams Lake in the Cariboo Region of central interior British Columbia. The closest town to the mine, located at the outlet of Quesnel Lake, is Likely.

Quesnel Lake is believed to be among the deepest fjord lakes in the world, reaching an estimated maximum depth of 511 m (Laval et al. 2008). The lake is an important habitat for multiple species of salmon and resident fish populations such as rainbow trout (Petticrew et al, 2015). Many aquatic species hold cultural and spiritual significance for the First Nations populations, as well as support commercial, recreation and aboriginal fisheries. The lake is located approximately 9.2 km downstream from the Mount Polley mine site and at the time of the tailings storage facility failure in August 2014, sockeye salmon of the Fraser River run were making their way upstream to their primary spawning habitats in the Mitchell and Horsefly Rivers. An estimated ~822,000 sockeye of the dominant four-year life cycle returned to these waters following the breach. This number is in addition to juveniles of the 2013 cycle who were still in the lake at the

time of tailings spill (Petticrew et al, 2015). Studies on salmon in hatcheries have indicated that copper can induce olfactory toxicity which is of relevance because wild populations use these senses for navigation to their spawning grounds (Baldwin et al, 2011; Wang et al, 2013; Sandahl et al, 2006). Because of the multiple-year life cycle of salmon, it is too early to confirm what the effects of the tailings loaded into Quesnel Lake have been on the aquatic populations.

The terrestrial area around the Mount Polley mine site is categorized under the bio-geoclimatic ecological classification as Interior Cedar – Hemlock forest (B.C. Ministry of Forests, Lands & Natural Resource Operations, 2014). It also falls within the western reaches of the Interior Temperate Rainforest. This broader region has been described as one of the few remaining tracts of land where large, iconic mammalian species, such as grizzly bears, mountain caribou, cougar, lynx, wolf, wolverines have their habitat (Craighead et al, 2008). Numerous browsing animals roam the forests and creeks around the Mount Polley mine feeding off of foliage, berries and other food sources. Local first nation communities have for time immemorial collected medicines and subsistence foods from these lands. Blue huckleberry, red huckleberry, soapberry, labrador tea, deer meat, deer liver, moose meat, moose liver, salmon and resident fish species like rainbow trout are among the consumed traditional foods for the local First Nations peoples (Chan et al, 2011).

1.3 Mount Polley Mine and Tailings Storage Facility Failure

The Mount Polley mine is a copper and gold mine owned and operated by the Mount Polley Mining Corporation (MPMC), a subsidiary of Imperial Metals Corporation. Production first began in June 1997 and continued until 2001, when low metal prices forced the mine to close for a number of years. In March 2005, operations resumed, uninterrupted, until the tailings storage facility failure in the summer of 2014 (Figure 1.1).

The majority of the mine's facilities are located between Bootjack Lake and Polley lake. The mine processes ore predominately from an open pit with some additional underground mining. The ore is crushed, processed and milled onsite and a copper-gold concentrate is extracted through a process of selective floatation (Hoffman, 2015). This method produces waste in the form of a tailings slurry which is then transported by pipe to the tailings storage facility (TSF). The tailings storage facility covers approximately 2.4 km² in area and is located just southeast of the mine's other facilities adjacent to Hazeltine Creek.

Figure 1.1 NASA satellite imagery of Mount Polley mine facilities and the west arm of Quesnel Lake, with surrounding terrestrial landscapes. Upper image was taken on July 29th, 2014 and the lower image was taken on August 5th, 2014. NASA Earth Observatory images by Jesse Allen using Landsat data from the U.S. Geological Survey.



Overnight on August 4th, 2014, the dam wall enclosing the tailings storage facility collapsed, causing an uncontrolled breach that released between 21-25 million cubic meters of mine tailings slurry into the surrounding environment (Figure 1.1) (Hoffman, 2015). The tailings flowed into Polley Lake at the confluence of Hazeltine Creek, devastating the wetland ecosystem that existed there, and scoured a channel down to Quesnel Lake. Hazeltine Creek, which was an average 5 m wide and 0.3 m deep and hosted a number of ponds, beaver dams and a forest-riparian interaction zones (Golder Associates, 2015), was also entirely wiped out by the flow of tailings. Tailings covered some areas of the Hazeltine Creek channel with more than 3.5m and in other places, severely eroded the landscape leaving behind highly unstable slopes and exposed bedrock (Figure 1.2). Approximately 236 hectares were directly affected by the scouring and deposition of tailings and forest debris (Golder Associates, 2015).

Figure 1.2 Image of eroded landscape along Hazeltine Creek channel (June 2016).



1.4 Impact on Forest Vegetation

In the spring of 2015, many of the trees along the Hazeltine Creek channel that appeared to have survived the winter, died quickly. Initially, there was concern that the rapid dieback was caused by phyto-toxicity from elevated levels of copper and other trace metals in the tailings. A terrestrial risk assessment was conducted by Miller & Simard (2015) to identify the cause of the dying trees. Their investigations revealed that an anaerobic environment was created in the root zone after the tailings were deposited. They hypothesized that the trees changed their metabolism in the late summer of 2014 to survive the low oxygen conditions and entered premature winter dormancy. During the spring freshet of 2015, snowmelt, in combination with very limited pore space in the deposited tailings, made the root zone anoxic. As the roots began to die, the spring temperatures initiated photosynthesis in the trees. Since the dying roots were unable to acquire the necessary oxygen or water, the trees very rapidly died (Miller & Simard, 2015).

Understanding the trees physiological response to the tailings deposition continues to be very important for ongoing restoration. The results from Miller and Simard (2015) indicated that the physical growing medium, even for very well-established vegetation, is very poor. Physical properties, coupled with elevated concentrations of a number of trace metals including copper, selenium and vanadium, may impact root systems, foliage and fruit quality of future vegetation. Ongoing research regarding the quality of vegetation and the accumulation of metals in different parts of the ecosystem is important for minimizing metal toxicity, impaired functioning and structure of the ecosystem. Abnormalities at the microorganism and invertebrate species level can be felt around the biotic network causing adverse health effects to many higher-level organisms (Fedotov & Miro, 2008).

1.5 Impact on First Nations Communities

This impact of the TSF failure has had lasting effects on more than just the immediate receiving environment. The First Nations Health Authority has identified four major health concerns experienced specifically by nearby First Nations communities following the tailings storage facility breach (Shandro et al, 2016). They include:

- **“Emotional stress”** is one of the fundamental health concerns shared by all twenty-two participating communities. Stress is felt in relation to the severity of the tailings

storage facility failure, uncertainty about the longer-term consequences and skepticism with regards to the information being shared with communities following the spill.

- **“Direct impact to traditional territories”** that prevents the Xat’sull, T’exelceme and Lhatko Dene First Nation from accessing sacred lands and territories, traditional food sources and medicine.
- **“Decrease in personal fishing practices”** which means that there have been significant shifts in nearly all the communities’ diets, physical activity and cultural practices.
- **“Impacts to commercial fisheries”** that have affected six communities’ income and employment opportunities

1.6 Geology and Soils of the Study Area

The ore at the Mount Polley mine is characterized by an alkalic porphyry copper gold deposit (B.C. Ministry of Energy and Mines, 2013). The dominant rock type ranges from diorite to syenite. Both are coarse grained igneous rock, the former is principally composed of plagioclase feldspar, biotite, hornblende, and pyroxene and the latter is dominantly alkali feldspars and various ferromagnesian minerals. The mineral alteration is potassic, propylitic and oxidation (B.C. Ministry of Energy and Mines, 2013). The sulphide component of the tailings has varied from ~33% - 80% throughout the years and it consists primarily of chalcopyrite (CuFeS_2) and pyrite (FeS_2), with some bornite (Cu_5FeS_4), covellite (CuS), and digenite (Cu_9S_5) (Kennedy & Day, 2015).

The dominant soils around the tailings impacted Hazeltine Creek channel are luvisolic humo-ferric podzols (Soil Survey Report No. 23) and generally have a profile with the following horizons: LFH, A_e, B_f (Al & Fe), B_t (silicate clays), C (Soil Classification Working Group, 1998). In the scour zones of the spill site the native soil has been buried, leaving the relatively unweathered, raw tailings exposed to the natural oxidizing conditions of the atmosphere. The depth of deposition is variable, ranging from approximately 1-3+ meters.

At the time of sampling (June 2016), it was evident that a significant amount of remediation work had been conducted in the lower Hazeltine Creek area. Some of the tailings had been removed, portions had been mixed with stockpiled till material, coarse woody debris had been

incorporated and used to cover other areas where the tailings had not been removed. The Hazeltine Creek channel had been re-contoured, numerous species of native vegetation planted, and two sediment ponds were being used to slow the flow and hold water before being diffused into Quesnel Lake at 45m and 50m depth (Golder Associates, 2016).

1.7 Geochemical Alteration of Tailings Under Atmospheric Conditions

During the mining process, ore is typically crushed, ground and milled to separate the small fraction of desired trace metals from the remainder of the gangue minerals. The unwanted material following the metal-recovery process makes up the solid fraction of tailings. At many low-grade mine sites, solid tailings represent vast quantities (upwards of 99% of the original material) of finely-ground rock that must be stored indefinitely in tailings impoundments (Lottemoser, 2003). Once deposited, the tailings undergo physical, chemical and biological processes that remarkably alter the mineral assemblages and elemental associations of fresh tailings (Blowes et al, 1991; Dold & Fontboté, 2001; Johnson et al, 2000). Tailings material generally has a much smaller particle size and thus larger surface area than the original ore, potentially exposing it to accelerated weathering. However, the uniform grain-size and subsequent hexagonal close packing upon deposition, may limit the rate of oxidation reactions because reduced permeability slows the movement of water and oxygen through the material (Ljungberg & Öhlander, 2001). Additionally, climate fluctuations impact the downward migration of leached solutes and capillary action during high surface evaporation, thus, they provide controls for weathering intensity, the formation of secondary minerals and the mobility of metals from tailings minerals (Dold & Fontbote, 2001; Berger et al., 2008).

The microbial ecology of the tailings environment also impacts the geochemistry of tailings minerals through bioweathering. This process, facilitated by bacteria, archaea and fungi can be described as the as “the erosion, decay and decomposition of rocks and minerals” (Burford et al., 2003). Similar to the rate-controlling factors of chemical weathering processes, biological mineral weathering rates are dependent on temperature, pH, and mineral as well as solution composition (Banfield et al., 1999). Biologically assisted degradation of minerals is controlled by mechanical and chemical processes. Fungal hyphae and lichen, work together with freeze-thaw cycles, to penetrate mineral cleavages and grain boundaries. The mechanical breakup of mineral surfaces is

further facilitated by the excretion of organic acids that actively dissolve mineral assemblages (Banfield et al., 1999). Exudates, with metal-complexing properties, are released by microorganisms and have profound implications on metal speciation, solubility, mobility, bioavailability and toxicity (Gadd, 1999)

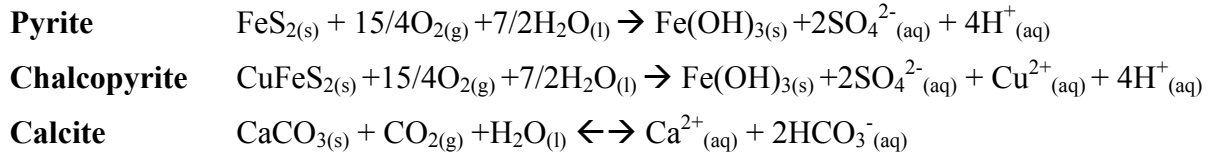
Weathering reactions can be acid producing or acid buffering in nature (Lottermoser, 2003). As pyrite weathers, it generates acidic conditions by producing H^+ ions, whereas when calcite minerals weather they consume H^+ , thereby buffering acidic conditions. At any given time, the balance between these reactions determines if the products of weathering are acidic. In strongly reduced media, the creation of insoluble metal sulphide precipitates can limit the bioavailability of many metals (Kotuby-Amacher & Gambrell, 1988). However, sulphide mineral oxidation and particularly pyrite oxidation, can result in acid rock drainage (ARD), which produces acidic effluent that is burdened with heavy metals (Dold & Fontboté, 2001). Acid rock drainage is among the greatest environmental challenges faced by the mining industry (Lottermoser, 2003).

Table 1.1 Minerals composition of selected tailings samples from Hazeltine Creek, identified by QEMSCAN and XRD analysis conducted by SRK Consulting. Table adapted from (Kennedy & Day, 2015).

	Minerals identified by QEMSCAN & XRD	
Silicates	Microcline (K-feldspar) Albite (Plagioclase) Anorthite (Plagioclase) Chlorite Quartz Diopside (Pyroxene) Muscovite	Adradite (Garnet) Grossular (Garnet) Almandine (Garnet) Kaolinite Epidote Titanite Biotite
Sulphides	Pyrite Chalcopyrite Bornite	
Carbonates, Oxides, Phosphates	Magnetite Calcite Hematite Fluorapatite Malachite	Dolomite (Fe) Malachite Apatite

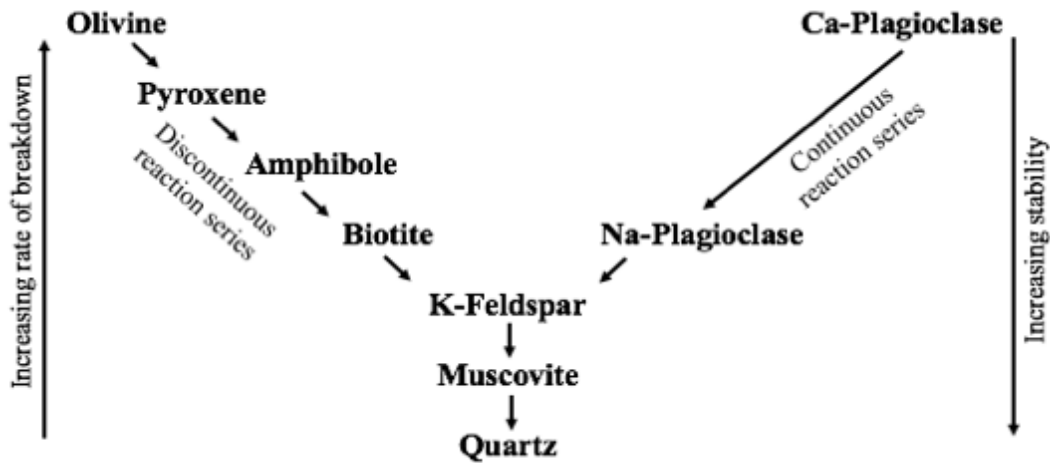
Acid buffering is largely facilitated by the weathering of carbonate minerals (e.g. calcite, dolomite), silicates (e.g. pyroxene, amphiboles, feldspars), hydroxides, and phosphates (e.g. apatite) (Sherlock et al., 1995). The presence of calcite greatly enhances the capacity of buffering reactions because it is rapidly converted to bicarbonate (HCO_3^-) and carbonic acid (H_2CO_3) through the dissolution and complexation of H^+ ions (Stumm & Morgan, 1995). When exposed to CO_2 , as is the case when in contact with surface and pore waters, the rate of dissolution of calcite increases compared to “closed system dissolution” where CO_2 is unavailable for gas exchange and thus calcite dissolution proceeds more sparingly (Sherlock et al., 1995).

As an example, the oxidation reactions for pyrite, chalcopyrite and calcite (in an open system) are given below:



It is well accepted that different minerals do not weather at the same rate (Figure 1.3) (Goldich, 1938; Srodon et al., 2014). Minerals such as olivine and anorthite are less stable and far more reactive at surface conditions than biotite, K-feldspars and muscovite.

Figure 1.3 Bowen’s reaction series (adapted from Buol et al., 1989).



Mineral rates of alteration are strongly dependent on the types of bonds linking elements together within mineral assemblages. The internal linkages between atoms in combination with chemical, physical and biological factors determine how quickly and easily minerals degrade. Poorly crystalline or minerals with structural imperfections are more susceptible to chemical

attack, as are those with trace element substitution (Hutchison and Ellison, 1992). Mineral solubility is given by a saturation index (SI) where:

$$SI = \log IAP / K_{sp}$$

IAP is the ion-activity product and is the product of elemental activities. It considers ionic strength, temperature and formation. The solubility product (K_{sp}) is the maximum possible equilibrium solubility given in the literature. When $SI < 1$ minerals will dissolve, $SI > 1$ causes them to precipitate and when $SI = 1$ the mineral and solution are in equilibrium (Sherlock et al, 1995; Merkel & Planer-Friedrich, 2008).

Silicate minerals make up the vast majority of the earth's crust. They consist of silicon and oxygen atoms orientated in a tetrahedron arrangement and bound by cations such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} or Fe^{3+} . These cations can be replaced by others with similar coordination numbers and ionic radii (Weil & Brady, 2016). Aluminum is a common substitute for silicon in the tetrahedron. Sheet silicates, also referred to as phyllosilicates, consist of tetrahedral and octahedral layers held together by Van der Waals forces. This important group of minerals includes micas, chlorites, serpentines, and clay minerals that are the primary products of chemical weathering (Blanchard, 1968).

Silicate dissolution can be congruent or incongruent. The right side of the Bowen reaction series (Figure 1.3) represents the incongruent dissolution of silicates by which minerals alter from one solid phase to another rather than being converted to soluble components. With time, mineral weathering can result in the formation of new minerals, secondary phase precipitates and soluble elements. Imagery techniques, like X-Ray Diffraction and Electron Microscopy have allowed researchers to observe bulk mineralogical changes in silicate weathering.

1.8 Metals in the Soil

The transportation of metals through soil solution, creeks, rivers and lakes is controlled by reactions that take place at the surface of soil colloids and is determined by the amount and form of specific metals, the soils physical and chemical properties as well as the composition of the soil solution (Turekian, 1977; Kotuby-Amacher & Gambrell, 1988). Soil texture, bulk density, surface area, particle size distribution, type and amount of metal-oxides, pH, redox potential, ion exchange

capacity, amount of organic matter and clays are useful soil properties for predicting the migration of elements through soils (Korte et al., 1976; Fuller & Warrick, 1985). Shuman (1991) described metals in the soil matrix as being present:

- dissolved in the soil solution
- on exchange sites on inorganic soil constituents
- adsorbed to inorganic soil constituents
- complexed with insoluble soil organic matter
- as precipitates
- within the structure of secondary minerals
- within the structure of primary minerals

Typically, metals associated with the first five pools are the most important when considering the possible migration of metals in the environment (McLean & Bledsoe, 1992). Over the long-term, those in the last two pools can gradually become available as weathering releases elements from within the mineral structure allowing them to enter the aqueous fraction. In soil solution, metals exist as soluble metal complexes with inorganic or organic ligands, as free ions, or attached to inorganic or organic colloidal material (McLean & Bledsoe, 1992). Metal complexation results in charge changes that affect the strength of adsorption to soil surfaces compared to free metal ions. The mobility, bioavailability and toxicity of metals depends on metal speciation with free metal ions often being the most bioavailable and toxic form (McLean & Bledsoe, 1992).

Many elements exist in multiple oxidation states affecting their mobility and toxicity (Violante et al 2010). For example, selenate (Se(VI)) is more mobile but less toxic than selenite (Se(IV)). Hexavalent Cr(VI) is toxic to plants, animals and humans and is relatively mobile and available in soils compared to Cr(III) which is less toxic and more readily adsorbed to surfaces and soil organic matter (McLean & Bledsoe, 1992; Violante et al., 2010; Fendorf, 1995). Copper(II) can be chemically reduced to Cu(I) by Fe^{2+} and H_2S (Borch et al., 2010), the latter forming Cu-rich sulphide compounds that can mobilize Cu, Pb, and Cd, though not necessarily solubilize them (Violante et al., 2010).

In soils, oxidizing conditions can decrease metal solubility (Page & Pratt, 1975) or increase the solubility and mobility of metals (Fuller, 1980; Bates, 1980), depending on the presence of sulphide or other redox compounds (Gambrell et al., 1980; Khalid et al., 1981). Metals can adsorb and co-precipitate with hydrous oxides making them important compounds for decreasing metal availability (Kotuby-Amacher & Gambrell, 1988). Most metal-sulphides also have very low solubility products (Violante et al., 2010). Where sulphides are absent, acidic and low redox potential conditions tend to favour more soluble, bioavailable and exchangeable forms of metals compared to alkaline and higher redox potential environments that promote sparingly soluble, oxidized compounds (Kotuby-Amacher & Gambrell, 1988).

The Mount Polley mine tailings contain predominantly carbonate, sulfide, and silicate minerals (Table 1.1) (Kennedy & Day, 2015; B.C. Ministry of Energy and Mines, 2013). These react with water and oxygen to produce water soluble elements and precipitates. Because the tailings are abundant in carbonate and silicate minerals with strong acid buffering potential, it has been presumed that the production of acidic leachates from sulphide oxidation will be limited (Kennedy & Day, 2015). However, carbonates and in particular, calcite, very quickly neutralize acid. In some extreme cases, the dissolution of calcite may even outpace that of pyrite causing otherwise neutral runoff to become increasingly acidic over time (Lottermoser, 2003). In the short-term, carbonates are important for determining the quality of drainage waters, however if carbonate and silicate co-exists, as is the case for the Mount Polley material, once the carbonate minerals are depleted, it is the long-term alteration of silicates that will act to neutralize acids (Sherlock et al, 1995).

1.9 Ecosystem and Human Health Concerns

Golder Associates (2017) articulates a response to the numerous human health concerns related to the ecological impact of the Mount Polley tailings storage facility failure. They identify three broad land-use categories within the immediately affected Hazeltine Creek channel: wildland, backcountry recreational areas and land that is a part of the Agricultural Land Reserve. The report acknowledges that the land will be accessed by people for recreation as well as food harvesting and that Quesnel Lake is used as a drinking water source for residential domestic water use (Golder Associates, 2017).

Golder Associates identified contaminants of potential concern (COPC) in the Detailed Site Investigation Update report (2017). They used the CSR standards for the protection of human health to determine the COPC and to decide which of the parameters needed to be considered in further risk assessment reports like the Human Health Risk Assessment (2017). Although the concentrations of potential contaminants in soil and tailings were not found to exceed the CSR standards for human health they did exceed the standards for the protection of soil invertebrates and plants for a number of metals. Human exposure to contaminants differs based on the medium (ie: soil, groundwater, sediment, surface water, and food source) and the type of interaction that a person has with that medium. Therefore, a First Nations traditional land user or a Quesnel Lake resident would be impacted differently by the tailings contamination along Hazeltine Creek and Quesnel Lake than a visiting recreational fisher.

Soil contaminants of potential concern in the tailings as identified in DSI report include copper (Cu), vanadium (V), sulfur (S) and molybdenum (Mo) (Golder Associates, 2016). The primary exposure pathways for copper, vanadium and aluminum as identified by Golder Associates (2017) are “incidental sediment and soil ingestion, dermal contact with sediment, soil and surface water, inhalation of soil particulates, ingestion of surface water and ingestion of berries, traditional plants, deer meat, deer liver, moose meat, moose liver, fish and grouse. The groundwater in Hazeltine Creek corridor has exceeded drinking water standards for iron, manganese, arsenic, molybdenum and sulfate (Golder Associates, 2017).

Meaningful restoration will need to fully recognize and address the physiological emotional, cultural and spiritual human health concerns, in addition to the ecological damage that the tailings storage facility failure caused. It is possible to estimate some of the ecological impacts to date, however, the long-term fate of the ecosystem and the species that depend its intricate balance remains largely unknown. This study takes a detailed look at the mineralogy of the tailings material and attempts to predict changes that will occur to the mineralogical surfaces over the long-term. The changes that take place at this level over geologic time scales are important because they impact the mobility, bioavailability and toxicity of heavy metals in the surrounding environment. This study sets the early stage of a longer-term dynamics of mineral weathering and release of potential toxic elements.

1.10 Objectives

The objectives of this study are to:

- 1) Characterize the chemical and physical soil properties of the tailings material along the Hazeltine Creek Channel from Polley Lake to Quesnel Lake.
- 2) Assess the effects of three acids (acid ammonium oxalate, hydrochloric acid, and *aqua regia*) on the composition and surface chemistry of the Mount Polley tailings material following laboratory simulations.
- 3) Discuss the significance of the Mount Polley mine tailings surface properties in relation to ecological and human health concerns.

Chapter 2: Assessment of the physical and chemical properties of the tailings material deposited along Hazeltine Creek, including a description of their capacity as a growing medium.

2.1 Introduction

The results presented in this chapter support the tailings characterization work executed by SNC Lavalin (2015) in the wake of the tailings storage facility failure of 2014. This chapter focuses on the edaphic characteristics of the tailings. Bulk density measurements were taken as an indicator of compaction, pH was recorded in H₂O and CaCl₂ to comment on the presence of free carbonates and the plant availability and mobility of nutrients, and the loss on ignition method was used as an index for organic matter concentration. The results provide a snapshot description of the tailings material as a growing medium for plants.

2.2 Sampling Locations

Nine locations were sampled for tailings and till along the Hazeltine Creek spill path of the 2014 TSF failure. Distance from the TSF breach at Polley Lake to the farthest sampling site at Quesnel Lake, is approximately 9 km (Figure 2.1). Five sites were selected in the vicinity of Polley Lake, in an area referred to as the Polley Plug. Here, it was estimated that tailings deposition exceeded 3.5 m (Golder Associates, 2015). Sites 6-9 were located between the banks of the re-channeled Hazeltine Creek and the adjacent forest. At each of the nine sites a 5 m x 5 m plot was delineated. Within the plot, seven samples were taken at random from the 0-15 cm depth and another seven were taken from the 15-30 cm depth.

Site 1 was located within 20 meters of Polley Lake. Sites 2-5 were located in the “Polley Plug” area between Polley Lake and the TSF. They were pure tailings samples. Site 6 was located under one of the remaining tree stands along the scour zone of Hazeltine Creek. Samples from Site 6 contained a mixture of organic material and tailings. Sample 7 and 9 were predominantly tailings material. Site 7 was about midway down Hazeltine Creek and Site 9 was located just before Hazeltine Creek and Quesnel Lake meet. Site 8 was located in the Lower Hazeltine area where a significant amount of restoration had been executed. The sample was a mixture of tailings and till, with some organic material.

Figure 2.1 Approximate sampling locations with brief characterization of the material composition of the selected samples



2.3 Materials and Methods

2.3.1 Bulk Density

In June 2016, seven bulk density samples were collected at 0-15 cm and 15-30 cm depth at each of the nine sites using the excavation or water replacement method. Samples were stored in sealed plastic bags and kept in a cooler until transported back to the laboratory.

Sample wet weight was recorded before opening the bags. A wet subsample of each was weighed in a clean, pre-weighed tin and the tins were then placed in the oven overnight at 105°C. The dry weight of the tins was recorded to determine percent moisture of the samples and to extrapolate dry weight of the bagged samples. Bulk density was determined using the dry weight of the samples and the volume of water poured into each sample hole in the field.

2.3.2 pH

The pH in water and in CaCl₂ were measured for all samples collected in June 2016 at the Mount Polley Mine spill site. The difference between pH measured in water and CaCl₂ gives an indication of exchangeable acidity; differences < 0.5 units indicate low exchangeable acidity. Ten g of tailings were weighed into a “Dixie Cup” was combined with 20 mL of distilled water. The suspension was stirred several times over 30 minutes then left to stand for 30 minutes, allowing the fine material to settle. A pH glass electrode was calibrated using two standard stock solutions of pH 4 and pH 7. The pH of the supernatant solution was measured by placing the electrode into the solution. The electrode was rinsed with distilled water between each measurement and the electrode was recalibrated against the standard solutions every 20 samples. Once all samples were analyzed, 20 mL of 0.02M CaCl₂ solution was added to the “Dixie Cup” and the procedure was repeated for pH measurement in CaCl₂.

2.3.3 Loss on Ignition

Approximately 7 g (0.001 g accuracy) of oven-dried (105⁰C) tailings were weighed into a clean, pre-weighed and labeled crucible. Crucibles were placed into a muffle furnace at room temperature. The heat was increased slowly (about 10°C / minute) to about 375°C. Temperature was maintained at 375°C overnight (~16 hours). The furnace was turned off and the crucibles were allowed to come to room temperature before being weighed again to nearest mg. The crucibles were then re-inserted into the muffled furnace and the heat was increased to 550°C. The temperature was maintained at this heat overnight (~16 hours). The furnace was turned off and again the crucibles were allowed to come to room temperature before being weighed to the nearest mg (Kalra & Maynard, 1991).

2.4 Results and Discussion

2.4.1 Bulk Density

Table 2.1 gives the mean bulk density values recorded per site. A number of these represent values that are notably higher than they should be. For example, mean bulk density at site 2 (15-30cm) of 4850 kg/m³. It was not possible to obtain accurate bulk density calculations for many of the subsamples of Site 2 because the site was quite wet and the tailings had very little cohesive strength thus giving them the tendency to flow. All calculated bulk density values that exceeded 2,650 kg/m³ (assumed particle density) were omitted from the data set for statistical tests because they were impossible observations and represented a sampling error.

Bulk density (BD) of a typical mineral soil generally ranges between 1,100 -1,500 kg/m³ (Weil & Brady, 2016). Higher bulk density is observed in compacted soils and at depth. Bulk density is inversely related to porosity. Porosity estimate is given as:

$$\% \text{ porosity} = 1 - \text{BD}/\text{PD} \times 100\%; \text{ assuming a particle density (PD) of } 2650 \text{ kg/m}^3.$$

This would mean a porosity of ~ 40 % if BD is 1500 or a porosity of ~ zero if BD is approaching 2650 kg/m³. % porosity = 1 - BD/PD x 100%; assuming a particle density (PD) of 2650 kg/m³. Soil porosity describes the volume of void or ‘empty’ space within total soil volume. Described as a percentage, a higher porosity reflects more available pore space for water and oxygen to move through the soil matrix.

A paired two-sample t-test for means demonstrated that although bulk density decreased marginally with depth from M = 1,730 kg.m³ (SD = 0.25) to M = 1,700 kg/m³ (SD = 0.25), this change was not significant $t(8) = 0.38$ $p = 0.36$. An ANOVA Single Factor Test performed using R Studio revealed significant difference ($p= 0.005$) between BDs at Site 2 and 8 for the 0-15 cm depth, however, only minor variations were observed among other sites for the 15-30 cm range ($p = 0.060$).

The tailings material generally has a very uniform particle size as a result of the crushing and grinding that occurs during ore processing. This results in what is assumed to be hexagonal close packing. Bulk density values observed in the tailings sampled from the Mount Polley mine spill site are variable. Pore space is limited due to the compaction that occurred during deposition. It is expected that during the spring freshet when water is abundant, ponding may occur as infiltration and percolation through the tailings is limited where high bulk density was observed.

Root growth through this material will also likely be restricted and may be worsened by poor aeration through the tailings material. A decrease in bulk density can be achieved by increasing the organic matter content of soils and encouraging processes that support aggregation.

2.4.2 pH

Mean active pH per site, expressed by pH in water, ranged narrowly in the 0-15 cm depth from 7.64 to 8.17 and between 7.25 to 8.28 in the 15-30cm depth. A paired two-sample t-test for means showed that $\text{pH}_{(\text{H}_2\text{O})}$ decreased slightly with depth from $M = 7.92$ ($SD = 0.15$) to $M = 7.91$ ($SD = 0.33$), however, this change was not significant $t(8) = 0.11$ and $p = 0.46$. The pH from Site 6, where tailings were mixed with some organic material from the forest floor, was the most acidic; results of an ANOVA Single Factor Test indicate that $\text{pH}_{(\text{H}_2\text{O})}$ differed significantly between sites for the 15-30cm depth ($p = 3.56\text{E-}8$) but not for the 0-15cm depth ($p = 0.311$). Site 6 was particularly set apart from the other sites, likely due to its higher organic matter content. Average pH, measured in CaCl_2 , ranged narrowly between 7.18 and 7.86 for the 0-15 cm depth and between 7.20 and 8.02 for the 15-30 cm depth. A paired two-sample t-test for means demonstrated that $\text{pH}_{(\text{CaCl}_2)}$ increased with depth from $M = 7.59$ ($SD = 0.21$) to $M = 7.66$ ($SD = 0.24$), but this change was not significant $t(8) = -1.12$ and $p = 0.15$. ANOVA Single Factor Test results indicated that $\text{pH}_{(\text{CaCl}_2)}$ differed significantly among sites for both 0-15cm and 15-30cm depth ($p = 0.007$ and $p = 3.61\text{E-}12$) respectively.

pH readings between 8.0 and 8.3 generally indicate the presence of free carbonates (Weil & Brady, 2016). Cementation of tailings layers has been recorded at a number of different mine sites and it is presumed to be due to the precipitation of secondary solids (Blowes et al., 1990; Boorman & Watson, 1976; McSweeney & Madison, 1988; Kennedy & Hawthorne, 1987). Increases in pH, which can be moderated by carbonate minerals, can enhance the precipitation of Fe(III) hydroxides and thus the formation of hardpan or cemented layers. In some instances, the formation of hardpan layers can act as a desirable physical and chemical barrier (Blowes et al., 1990). Cemented layers can restrict the transport of dissolved metals through the tailings profile and the entry of O_2 , thus limiting the extent of sulphide oxidation (Boorman & Watson, 1976; McSweeney & Madison, 1988; Kennedy & Hawthorne, 1987). Surface cementation was observed on site at the time of sampling, and occurred on the outer layer of the samples after air-drying them

in the laboratory. Successful germination and rooting may be a challenge onsite because of the restricting layer cause by the precipitation of secondary mineral.

Kotuby-Amacher & Gambrell (1988) investigated the factors that affect metal mobility in subsurface soils. Metal cation immobilization was enhanced by increases in pH due to significant increases in adsorption capacity above pH 7 (Harter, 1983). The opposite effect is observed for anions i.e. arsenic, selenium, and hexavalent chromium. As the pH decreases, the number of negative sites for cation adsorption decreases as cations compete for permanent charge sites with H^+ and Al^{3+} ions (McLean & Bledsoe, 1992). Under alkaline conditions many metals form precipitates with oxides, hydroxides, carbonates and phosphates and these tend to dissolve as the pH drops below 6 (Essen & El Bassam, 1981; Lindsay, 1979).

Macro nutrient availability is also affected by pH levels. Phosphorus, an element required for photosynthesis, reproduction, and rooting in plants, is most readily available between pH ~6–7.5 (Weil & Brady, 2016). Under more acid and more alkaline pH conditions phosphorus availability is limited because of fixation with aluminum, iron and calcium. Micro nutrients too have optimal pH ranges where they are most plant available. In the alkaline tailings, it is presumed that many important nutrients will be tied up and unavailable for plants.

2.4.3 Loss on Ignition

Excluding Site 1 (0-15 cm range), data from loss on ignition measurements, indicated that when tailings were the dominant material (Sites 1-5, 7 & 9), the percent lost when heated to 375°C was less than 1.19%. Of the 7 samples collected from Site 1, one of them had a mound of what appeared to be either charred or partially decomposed organic matter incorporated with the upper layer of tailings. For this reason, and despite the site being predominantly comprised of deposited tailings, Site 1 resulted in a disproportionately high average percent loss on ignition compared to the other majority tailings sampling locations. In samples where the tailings were mixed with some organic matter (Site 6 & 8) the percent loss on ignition ranged between 2.53% and 7.73%. A paired two-sample t-test for means demonstrated that although the loss on ignition decreased with depth from $M = 2.49$ ($SD = 2.89$) to $M = 1.91$ ($SD = 2.43$), this change was not significant $t(8) = 0.55$ $p = 0.30$. ANOVA Single Factor Test results indicated no significant differences between sites in LOI from the 0-15 cm depth, however, within the 15-30 cm range, significant differences in LOI

were observed ($p = 8.97E-5$). Site 6 is distinguished from all others except Site 8 where tailings and till are intermixed. Excluding the outlier at Site 1 (0-15 cm) the majority tailings samples experienced marginal losses upon heating suggesting that the samples contain very little amounts of organic matter.

Loss on ignition analysis is a common, cost-effective method for estimating organic matter content in soils and sediment (Dean, 1974), however, its precision and accuracy have been questioned (Pallasser et al., 2013) and it is believed that it can over-estimate the amount of organic matter present by considering, in an undistinguishing manner, multiple losses (Veres, 2002).

Table 2.1 Summary of average results by site for bulk density, pH and loss on ignition analysis.

Site	Sample Type (depth)	Sample Size (n)	Bulk Density (kg/m ³)	pH (H ₂ O)	pH (CaCl ₂)	LOI 375° C (%)
1	Tailings (0-15cm)	7	1528	8.00	7.86	7.82
	Tailings (15-30cm)	7	1683	8.21	8.02	0.99
2	Tailings (0-15cm)	7	2537 ²	7.96	7.62	0.36
	Tailings (15-30cm)	7 (6) ¹	4850 ²	8.11	7.62	0.43
3	Tailings (0-15cm)	7	1601	8.17	7.82	0.47
	Tailings (15-30cm)	7	1755	8.28	7.91	0.45
4	Tailings (0-15cm)	7	1577	8.01	7.71	1.17
	Tailings (15-30cm)	7	1737	8.12	7.85	1.00
5	Tailings (0-15cm)	7	1767	7.88	7.49	0.72
	Tailings (15-30cm)	7	1629	8.00	7.66	0.59
6	Tailings with Organics (0-15cm)	7	1732	7.64	7.53	2.53
	Tailings with Organics (15-30cm)	7 (5) ¹	1195	7.25	7.20	7.73
7	Tailings (0-15cm)	7	1934	7.87	7.63	1.04
	Tailings (15-30cm)	7 (6) ¹	1707	7.78	7.58	1.18
8	Tailings with Till & Organics (0-15cm)	7	1373	7.94	7.46	7.09
	Tailings with Till & Organics (15-30cm)	6	1540	7.66	7.56	3.91
9	Tailings (0-15cm)	7	2307 ²	7.81	7.18	1.19
	Tailings (15-30cm)	7	2573 ²	7.80	7.54	0.83

¹ Sample size for bulk density is within brackets

² Bulk density results are unadjusted and reflect higher than expected values due to a method selection that was inappropriate for the flowing nature of the tailings.

2.5 Conclusions

Overall, these results suggest that the tailings material that spilled from the TSF and was deposited along Hazeltine Creek is a very poor growing medium. The relatively high bulk density values, and thus, low porosity likely represent significant challenges for plant growth. Water movement through the material would also be expected to be slow, particularly in the late spring, following the freshet, and it is likely that conditions below the surface would be anaerobic or possibly anoxic. However, this study also demonstrated that under saturated conditions, like those at Site 2 during the time of sampling, the excavation method was inadequate for obtaining accurate BD calculations.

An important consideration is that these results represent the soil property characteristics of the tailings, at the time of sampling. The information provided is valid for a snapshot in time and does not reflect how, nor the degree to which, these properties will change over time. As the alkaline material weathers, it will become more acidic. Over time, organic matter will be incorporated by vegetative inputs and microorganism activity. This should improve the structure of the growing medium and increase aeration porosity through the material.

Adsorption capacity of cation metals in soils is correlated with a number of soil properties including pH, redox potential, Fe and Mn oxides, clays, soil organic matter, and calcium carbonate content while anion adsorption is primarily correlated with the former three (McLean & Bledsoe, 1992). Stable complexes formed between metals and soluble organic matter may increase metal mobility and the formation of secondary minerals precipitates may encourage crust development on the surface. The mobility and availability of metals and essential nutrients will shift with the dynamics of the oxidizing environment. It is premature to say how the interaction of all these alterations will affect future ecosystem health along Hazeltine Creek and in the Quesnel River Basin watershed.

Chapter 3: Acid treatments of tailings and till to simulate natural weathering processes and long-term metal mobility and bioavailability at the Mount Polley spill site.

3.1 Introduction

Mine tailings are fresh geologic materials; thus, they are unweathered and are susceptible to chemical changes in the oxidizing environment when exposed to earth surface conditions. Restoration efforts at the Mount Polley mine spill site must take into account not only the present chemical composition and condition of the deposited material but also the possible changes in composition under more weathered conditions that will occur over time. Simulation experiments in the laboratory using various acid treatments allow for the characterization of the tailings under such conditions. This chapter's aim is to comment on the surface reactivity of the tailings as well as the mobility and availability of nutrients and metals. The objectives are firstly, to compare three different acids (acid ammonium oxalate, hydrochloric acid, and *aqua regia*) in their ability to alter tailings deposits and secondly, to examine the extent of spatial variability in the chemistry of the tailings deposits with depth and along Hazeltine Creek from the TSF to Quesnel Lake.

3.2 Materials and Methods

Tailings samples were collected at the Mount Polley mine in June 2016. The same samples that were used for bulk density analysis were subjected to acid treatments to simulate the impact of weathering in the laboratory. All 126 samples collected on site were treated with 1.0 M hydrochloric acid and analyzed using ICP-OES. The variability within each site and at each depth was less than 10% so it was decided that for the other two acid treatments, three composite samples per site and depth would be analyzed, for a total of 54 samples, for the acid ammonium oxalate and *aqua regia* treatments. Each acid treatment was conducted independently on fresh (previously untreated) samples.

3.2.1 Acid Ammonium Oxalate Extraction

Acid ammonium oxalate extractions are recommended in soil analysis studies for the removal of poorly crystalline material, amorphous inorganic and organically complexed forms of

iron, aluminium and manganese (McKeague & Day, 1966; Ross & Wang, 1993) and for the dissolution of some specific minerals like magnetite (Chau & Zhou, 1983). It is a relatively weak acid (pH 3), however, as a complexing agent with strong chelating properties it is able to dissolve ions associated with amorphous materials and coatings, especially those associated with iron oxides (Smith, 1994). The treatment is used in this study to estimate the proportion of elements in the bioavailable fraction because living organisms all release oxalic acids.

For each of the 9 sampling locations, composite samples from the 0-15cm and 15-30cm depth were prepared for treatment with acid ammonium oxalate (McKeague & Day, 1966). Samples were ground using a porcelain mortar and pestle. Three 0.500 g tailings samples from each depth and site were weighed into 50 mL, acid-washed, screw-top containers. Each 0.500 g sample was treated with 25 mL of acid ammonium oxalate and shaken in the dark for four hours using a reciprocal shaker with 5 cm distance interval at 60 cycles per minute. Samples were transferred into acid-washed test tubes and centrifuged for 20 minutes at 510 x g. The clear supernatant was decanted into an acid-washed container and refrigerated until being analyzed for bioavailable elements using ICP-OES.

3.2.2 Hydrochloric Acid Extraction

Hydrochloric acid is a stronger acid than acid ammonium oxalate. It has a pH of 1 and dissolves the most easily weatherable minerals. The treatment is used in this study as an assessment of the most mobile elements in the tailings material. Theory suggests that hydrochloric acid treatment dissolves calcareous materials with the Cl^- acting as a strong ligand. It should solubilize elements associated with the non-residual phase and metals on exchange sites (Leleyter et al., 2012).

All samples collected in June 2016 were prepared for treatment with hydrochloric acid (Snape et al., 2004). Approximately 10.000 g of tailings were weighed into a 100 mL centrifuge tube. 50 mL of 1.0 M HCl was added and the mix was shaken for 1 hour using a reciprocal shaker with 5 cm distance interval at 60 cycles per minute. The suspension was quantitatively transferred into 100 mL volumetric flasks, previously fitted with Whatman #42 filter paper. Flasks were made to volume with 4% HNO_3 . The filtrate was transferred to acid washed containers and refrigerated until being analyzed for weatherable elements using ICP-OES.

3.2.3 Aqua Regia Extraction

Aqua regia is a common, EPA recognized method to estimate total recoverable elements in a sample, with the exception of those held within aluminosilicate compounds (Chen & Ma, 2001). It is a widely used, standardized, method for sediment and soil analysis and is particularly useful when determining the content of potentially harmful heavy metals (ISO 11466 1995). It should be noted that, when describing total recoverable elements in tailings, as extracted by *aqua regia*, it is not equivalent to, or representative of, total metal concentration. In order to assess total metal concentration an extraction with HF should be performed to completely release trace elements held within the aluminosilicate phases (Wilson et al. 1997). Notwithstanding this, for most metals (As, Cu, Fe, Hg, Pb, Zn) the difference in total and *aqua regia* extractable content is comparable (Sastre et al., 2002; Santoro et al., 2017).

Fresh composite tailings samples from each of the 9 sampling locations were prepared for the *aqua regia* digest method outlined by Chen & Ma (2001). Three replicates of approximately 0.5 g of each composite sample were weighed into a tared 500 mL Erlenmeyer flask. Analytical-grade concentration HCl and HNO₃ were mixed in a 3:1 ratio respectively to make the *aqua regia* solution. Twelve mL of *aqua regia* solution was added to each Erlenmeyer flask and then the flasks were heated on a hot plate at 110°C for 3 hours. An additional 5 mL of *aqua regia* solution was added and the mixture was heated almost to dryness. Twenty mL of 4% HNO₃ was added and quantitatively transferred to 100 mL volumetric flask, fitted with a funnel and Whatman #42 filter paper. Flasks were made to volume with dilute 4% HNO₃. The filtrate was transferred into acid-washed containers and kept refrigerated until being analyzed for total elements using ICP-OES.

3.2.4 Inductively Coupled Plasma – Optical Emission Spectrometer

Elemental concentrations of all acid digests were analyzed using a Varian 725ES Optical Emission Spectrometer from the University of British Columbia's Earth, Ocean and Atmospheric Sciences Department. Inductively coupled plasma emission spectrometers (ICP) are commonly used to determine total elemental concentrations in soil solution, although they do not distinguish elemental speciation or oxidation states (McLean & Bledsoe, 1992). The intensities of the dominant element wavelengths with best linear correlation were averaged and used to calculate concentrations of Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Se, Si, V and Zn.

3.2.5 Statistics

Given the heterogeneous composition of the sampled tailings deposit sites (tailings, till and organic matter) a decision was made to visually assess, using bar graphs, the variability among the sampling locations. The acid treatments were compared to one and other for their capacity to release elements from the tailings material. To do so, the standard deviation of the mean was determined and standard error was calculated using the equation: $SE = \text{Std Dev}/\sqrt{N}$. The standard error values were then used for error bars on the graphs. Microsoft Excel was used to make the bar graphs and R Studio was used for correlation and principal component analysis. A correlation table was made (p value = 0.01) to determine elemental correlation. Darker blue represents elements that are more positively correlated, while a darker red colour represents a negative correlation. The effect of depth on differences in elemental concentration was assessed using a paired two sample t-test for means in Excel. Principal component analysis was used to summarize the spatial variability in the elemental concentration data. Scatter plots were made to determine if element concentrations varied according to sampling location, material (tailings, tailings-till mixture, tailings-organic mixture) and depth.

3.3 Results and Discussion

3.3.1 Elemental Analysis

This section highlights the results of the three acid treatments and focuses on Cu, Cd, Cr, Pb, Zn, Se, V and P because some were raised as elements of concern and others were observed in elevated concentrations in the tailings samples. They will be discussed in comparison to the Contaminated Sites Regulation (CSR) standards for Wildlands Natural (WL_N). These standards are determined using an *aqua regia* extraction.

3.3.1.1 Copper (Cu)

Where tailings are the dominant sample material (Sites 1-5, 7 & 9), mean concentrations of total recoverable Cu ranged from 695 ppm to 1084 ppm (Figure 3.1). Mean bioavailable Cu, determined using acid ammonium oxalate, ranged between 219 ppm and 528 ppm. When treated with hydrochloric acid, the majority tailings samples (Sites 1-5, 7 & 9), released per site, between

241 ppm and 467 ppm Cu from the 0-15 cm depth and between 201 ppm and 419 ppm from the 15-30cm depth. There was no observable difference with depth (Figure 3.1 and 3.2). Where tailings were mixed with till and organic matter (Site 8) the amount of total recoverable Cu was notably less than for the other sites along Hazeltine Creek. There was also less bioavailable and mobile Cu at Site 8 than at the other sites. Extraction results suggested that Cu tends to be as soluble in hydrochloric acid as when chelated with oxalate. Both Figure 3.1 and 3.2 suggest that proximity to the TSF related to a slightly higher concentration of Cu. Depth did not have a significant impact on bioavailable or recoverable Cu, however a paired two sample t-test for means did show a significant decrease in mobile Cu (extracted with HCl) with increasing depth ($p = 0.01$).

Figure 3.1 Copper concentrations in acid-treated tailings samples (0-15 cm depth) from the nine sampling sites.

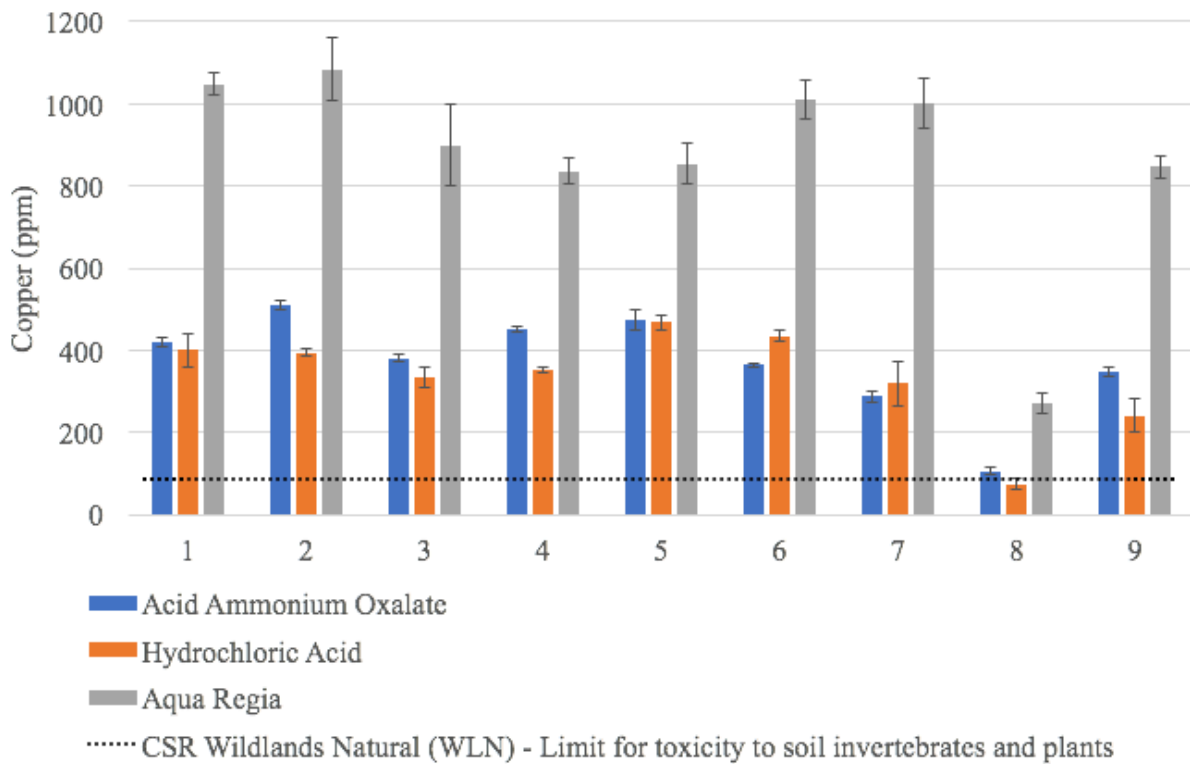
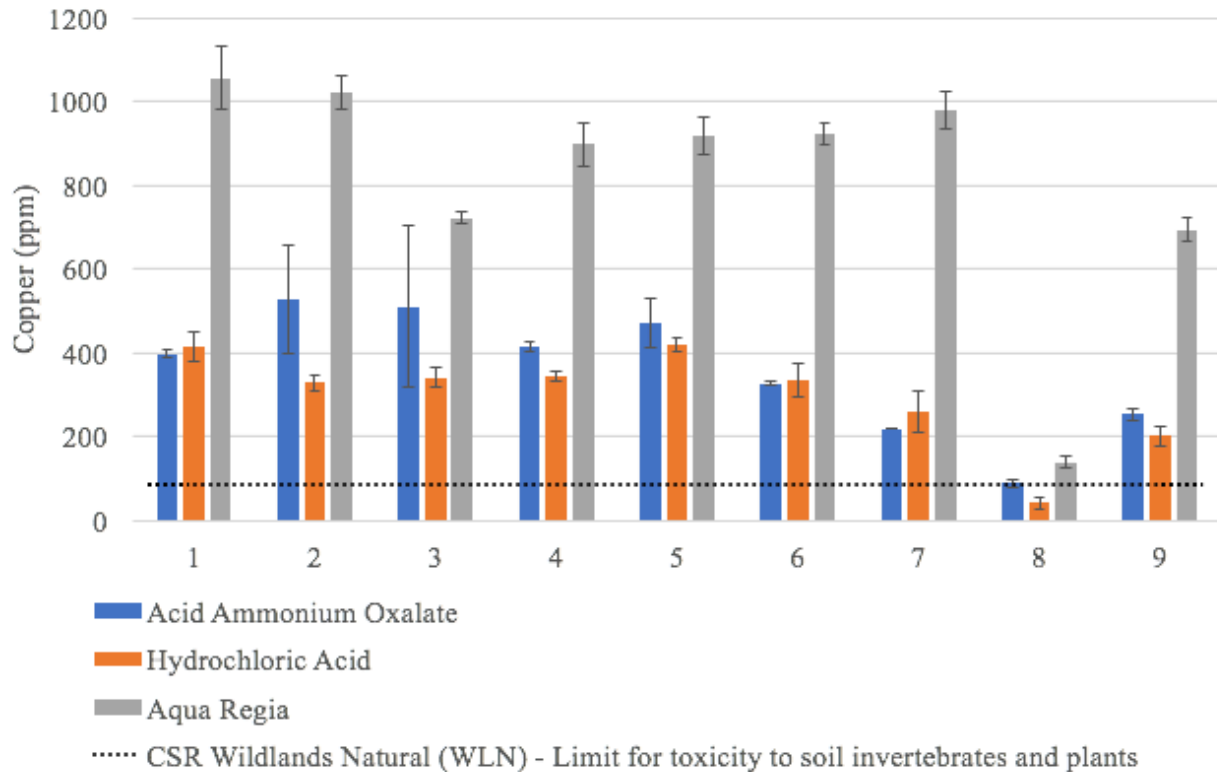


Figure 3.2 Copper concentrations in acid-treated tailings samples (15-30 cm depth) from the nine sampling sites.



Soil copper concentration for “toxicity to soil invertebrates and plants” under the Wildlands Natural (WLN) category of the CSR is 85 ppm. Under the agriculture land-use category 150 ppm and 350 ppm are given for the protection of “livestock ingesting soil and fodder” and “major microbial functional impairment” respectively (B.C. Ministry of Environment, 2017). These results suggest that the concentrations of bioavailable and mobile copper in the tailings could have the potential to disrupt ecosystem health and functioning. In calcareous soils, Cu concentration in solution may be controlled by the adsorption of Cu onto calcium carbonate molecules (McBride & Bouldin, 1984). It is observed here that as weathering progresses (increasing acid strength) and carbonate mineral dissolution proceeds, copper is released into solution making it increasingly available for root and microbial uptake.

3.3.1.2 Cadmium (Cd), Chromium (Cr), Lead (Pb), Zinc (Zn)

ICP-OES results from the three acid treatments, indicated that there are trace amounts of Cd, Cr, Pb and Zn present in the tailings. All concentrations observed were less than those outlined in Wildlands Natural (WL_N) category of the B.C. Contaminated Sites Regulation.

3.3.1.3 Selenium (Se)

The detection limit for selenium using the Varian 725ES Optical Emission Spectrometer is approximately 1 ppm. All the samples analyzed, included those treated with the strongest acid digest, *aqua regia*, were below the detection limit for Se concentrations. Selenium was a metal of concern because of toxicity in excess and because availability to plants and mobility increases under alkaline conditions (Fergusson, 1990). The extraction methods employed in this study utilized an open digest vessel, which may not be appropriate for elements like Se that volatilize when heated or shaken (Sastre et al., 2002).

3.3.1.4 Vanadium (V)

Vanadium appeared to readily form organo-mineral complexes and was markedly more soluble when chelated with oxalate than when treated with hydrochloric acid (Figure 3.3). Mean concentrations of bioavailable vanadium from tailings samples from sites (1-7 & 9) ranged from 152 ppm to 300 ppm for the 0-15 cm depth and 185 ppm to 386 ppm for the 15-30 cm depth. Where the tailings were mixed with till (Site 8), notably less V was extracted using acid ammonium oxalate 77 ppm and 57 ppm for 0-15 cm and 15-30 cm respectively. Less than 19 ppm was extracted from samples when treated with hydrochloric acid, suggesting that the most easily weathered minerals are not those that hold the majority of the vanadium, and instead that it is held by oxides and/or poorly crystalline minerals. Mean total recoverable vanadium in the tailings samples from sites 1-7 & 9 ranged from 321 ppm to 567 ppm. Samples from Site 8 (tailings mixed with till) had notably less recoverable vanadium at both the shallow and the deeper depths, 190 ppm and 117 ppm respectively.

Like Cu, there was markedly more, bioavailable and total recoverable V in the samples that are primarily tailings than those mixed with till material. A slight trend correlated proximity to the TFS and higher vanadium bioavailability and mobility; depth of sampling did not significantly

effect vanadium concentrations ($p = 0.33$, $p = 0.33$, and $p = 0.15$ for the acid ammonium oxalate, hydrochloric acid and *aqua regia* extractions, respectively).

Figure 3.3 Vanadium concentrations in acid-treated tailings samples (0-15 cm depth) from the nine sampling sites.

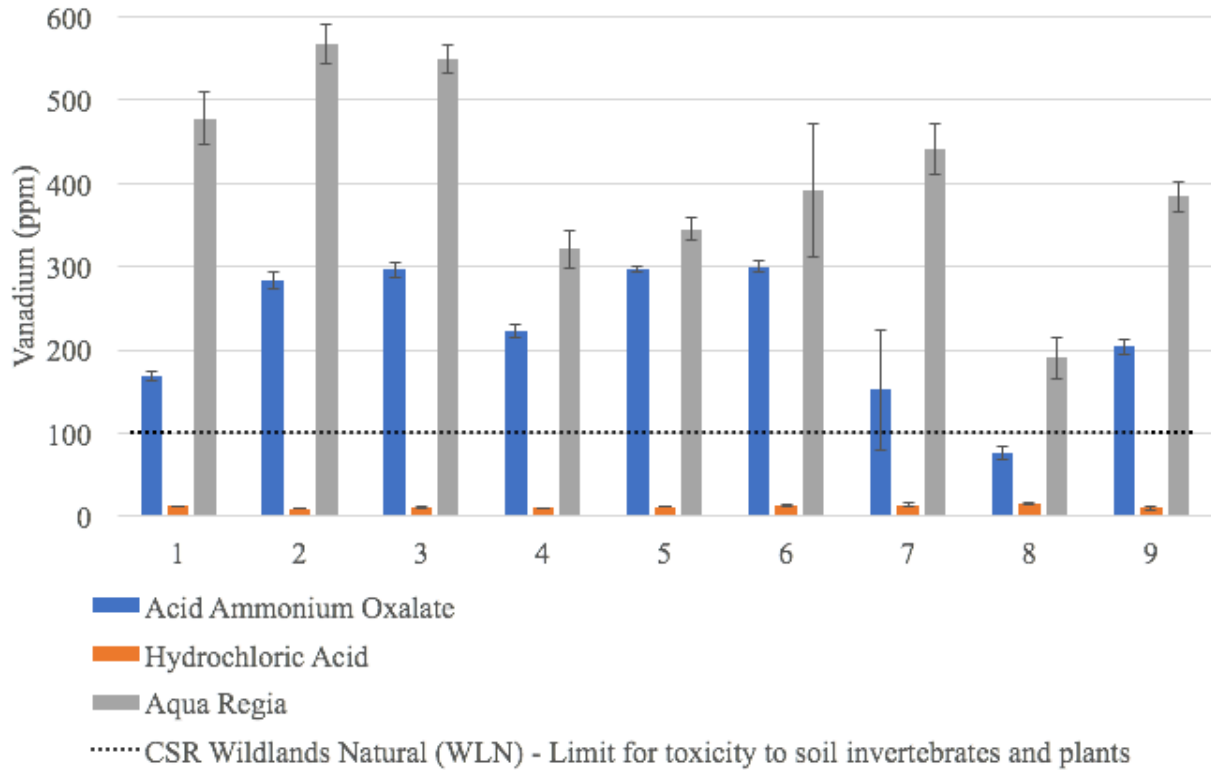
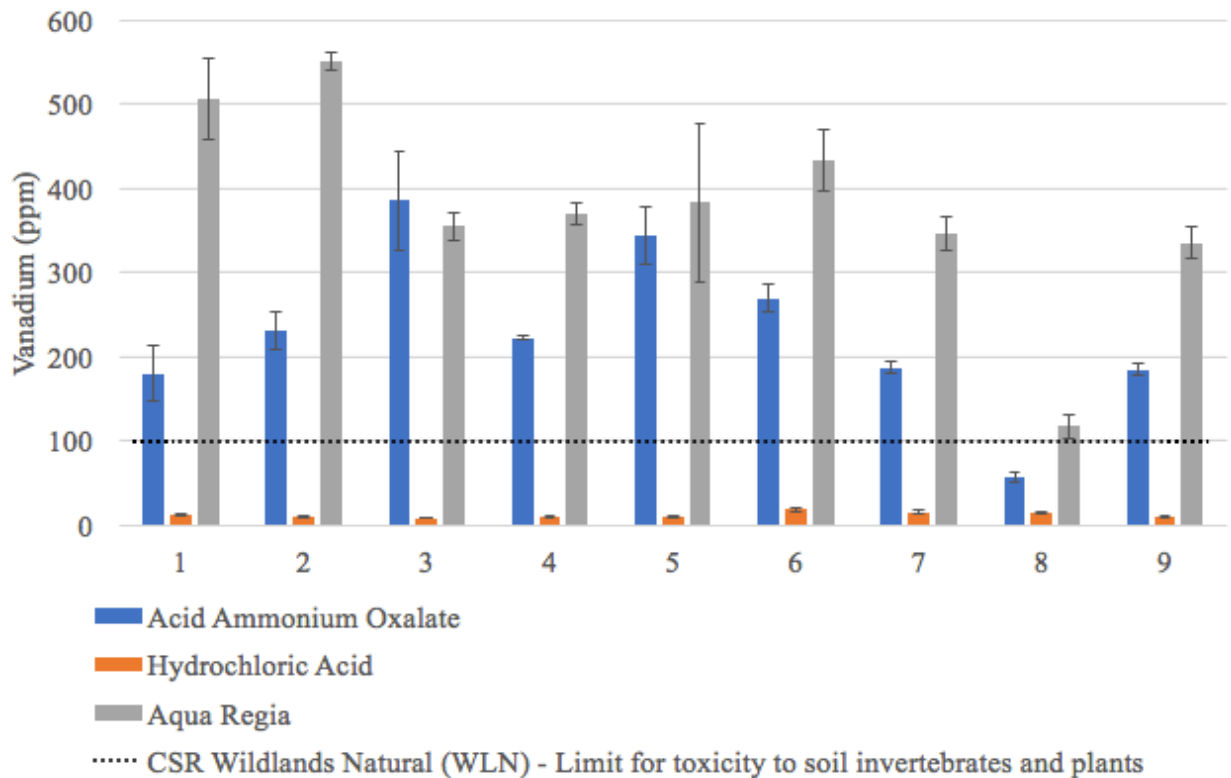


Figure 3.4 Vanadium concentrations in acid-treated tailings samples (15-30 cm depth) from the nine sampling sites.



Under the Wildlands Natural (WLN) site factor of the CSR, 100 ppm vanadium is the environmental protection limit for “toxicity to soil invertebrates and plants” and 400 ppm is the human health protection concentration for soil ingestion. Under the agriculture land-use category, 250 ppm is the upper limit for “major microbial functional impairment” (B.C. Ministry of Environment, 2017). These results suggest that the concentrations of bioavailable and mobile vanadium in the tailings could have the potential to disrupt ecosystem health and functioning.

3.3.1.5 Phosphorus (P)

Qualitative field observations made of Hazeltine Creek during the time of sampling inspired further analysis of phosphorus behaviour in laboratory treatments. Numerous sightings of algal blooms in the quick-moving Hazeltine Creek prompted intrigue as to levels of phosphorus and the origin of the phosphorus

ICP-OES results showed that phosphorus was far less soluble in oxalate than in hydrochloric acid as its chemistry does not readily lend itself to chelation (Figure 3.5). For the samples that consisted primarily of tailings (Sites 1-5, 7 & 9), mean phosphorus concentrations in samples treated with hydrochloric acid ranged from 727 ppm to 1242 ppm. This suggests that phosphorus forms fixed with carbonate and apatite minerals make up a significant amount of the total P in the tailings. Proximity to the TSF appeared to have an effect on P concentrations, trending towards lower P concentrations farther from the TSF. Site 8, where tailings and till are mixed, has notably less extractable P, likely because the till material is not enriched in P like the tailings. Depth of sampling did not affect concentrations of mobile or recoverable P, however a paired two sample t-test for means demonstrated reduced bioavailable P with depth ($p = 0.01$).

Figure 3.5 Phosphorus concentrations in acid-treated tailings samples (0-15 cm depth) from the nine sampling sites.

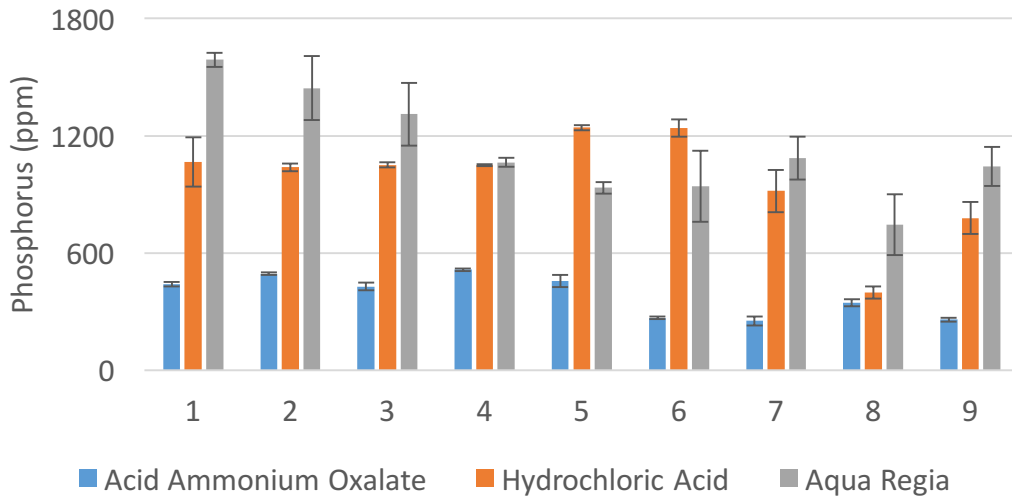
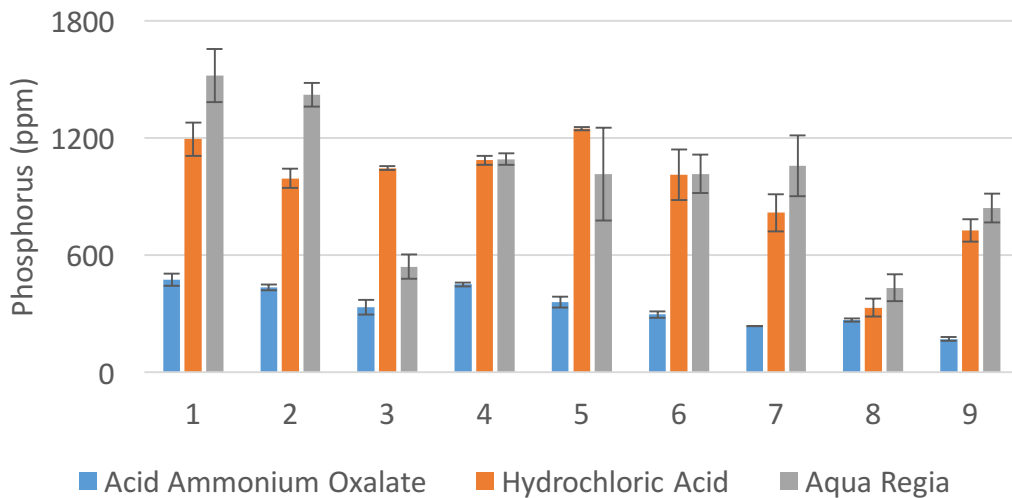


Figure 3.6 Phosphorus concentrations in acid-treated tailings samples (15-30 cm depth) from the nine sampling sites.



In theory, *aqua regia* should extract as much, if not more P, than the hydrochloric acid treatment. This was the case for most samples however there were a few sites, 5 & 6 (0-15 cm) and 3 (15-30 cm) where the HCl values are noticeable higher than the *aqua regia*. Plak et al. (2017)

used both HCl and *aqua regia* during a sequential extraction procedure examining the binding of arsenic and phosphorus in urban soils. *Aqua regia* was used to determine total phosphorus pool and in all instances, it exceeded the amount of P bound with calcium and apatite. It is possible that there was not enough HNO₃ in the *aqua regia* solution to completely oxidize the organically bound phosphorus in the Site 6 sample. Pre-treatment handling has been attributed with differences in the amount of P extracted and the relative amounts of P in different fractions when sequential extraction procedure are implemented (Condrón & Newman, 2011). Specifically, speculation exists regarding sample air-drying, maintaining sample anaerobic or aerobic field conditions for Fe-rich sediments and the effects that preparation methods have on extractability of P (Psenner & Pucsko 1988; Turner & Haygarth, 2003). Some evidence suggests that methods other than *aqua regia* may be superior for determining total P. Chandler et al. (2008) compared extraction methods for total heavy metals (Cr, Cu, Ni, Pb & Zn) and total P in four different contamination sources implementing the HNO₃ pressure digestion method and XRF for total P and only used *aqua regia* for metal extractions.

Phosphorus plays an essential role in the functioning, productivity and biogeochemical cycling of terrestrial and aquatic environments (Condrón & Newman, 2011; Jaisi & Blake, 2010). Excess phosphorus accumulation in aquatic ecosystems can cause dramatic, negative, environmental consequences as eutrophication disrupts the balance of receiving environments. The erosion of soil particles, with high phosphorus concentrations, into streams and lakes is an important contributor to eutrophication (Carpenter, 2005). Canadian soil quality guidelines for the protection of environmental and human health do not have any data for phosphorus. The water quality guidelines for the protection of freshwater aquatic species suggests developing “Trigger Ranges” for total phosphorus to monitor and predict nutrient enrichment (Canadian Council of Ministers of the Environment, 2004). From a fertility perspective, the concentrations of phosphorus observed in the three acid extractions are high (Weil & Brady, 2016).

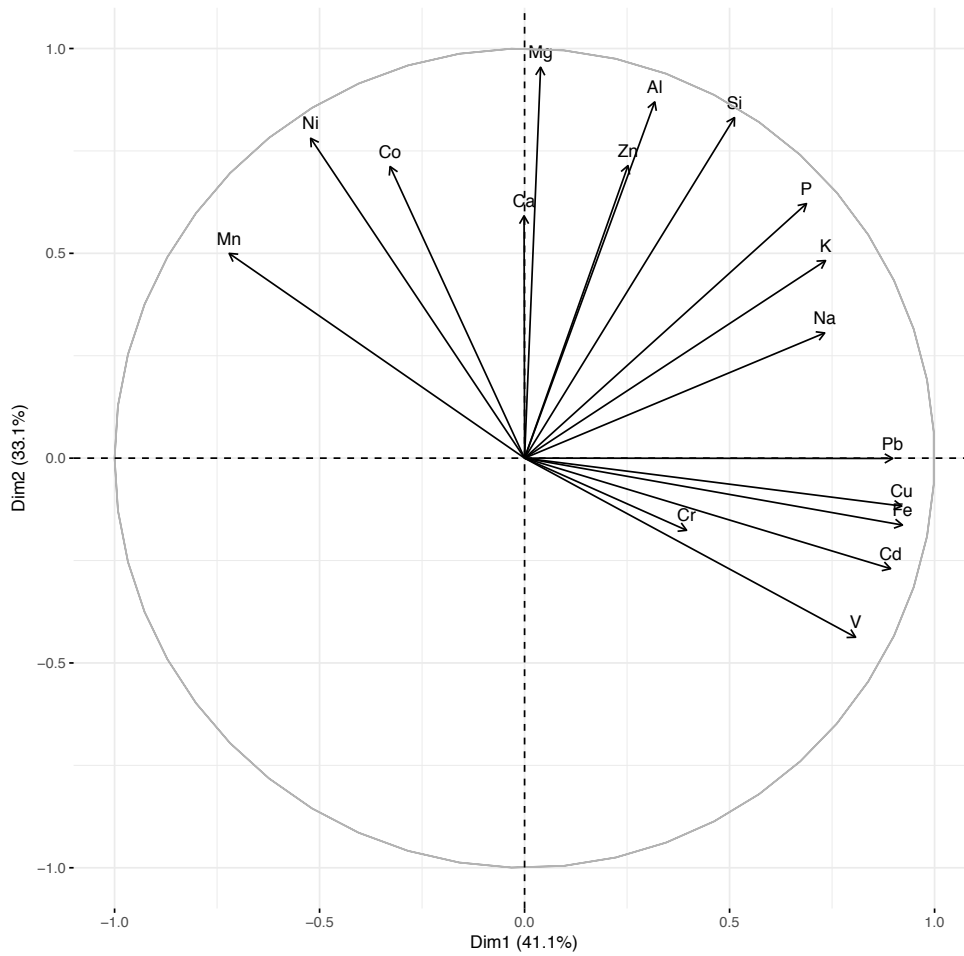
3.3.2 Elemental Correlation and Multivariate Analysis

A simple and common approach for conceptualizing mineralogical composition is to examine the distribution of individual elements relative to each other. The assumption is that the correlation of elements from an extraction may indicate that elements are bound to one another and may be released in a similar fashion under conditions of chemical weathering. Principal component analyses (PCAs) were performed to compare the relative chemical correlations for each extraction method. The strength of PCA is that multidimensional data can be reduced to two dimensions while much of the original information is retained (Singh & Agrawal, 2012).

A comparison of the PCA diagrams for the three different acid treatments (Figure 3.7, 3.8, 3.9), illustrates that when treatments are more selective, as is the case with acid ammonium oxalate, the result has greater variance in the ensuing chemical data (i.e. arrows for the different elements are more widely dispersed over a broader range of the correlation space). This implies less binding between individual elements.

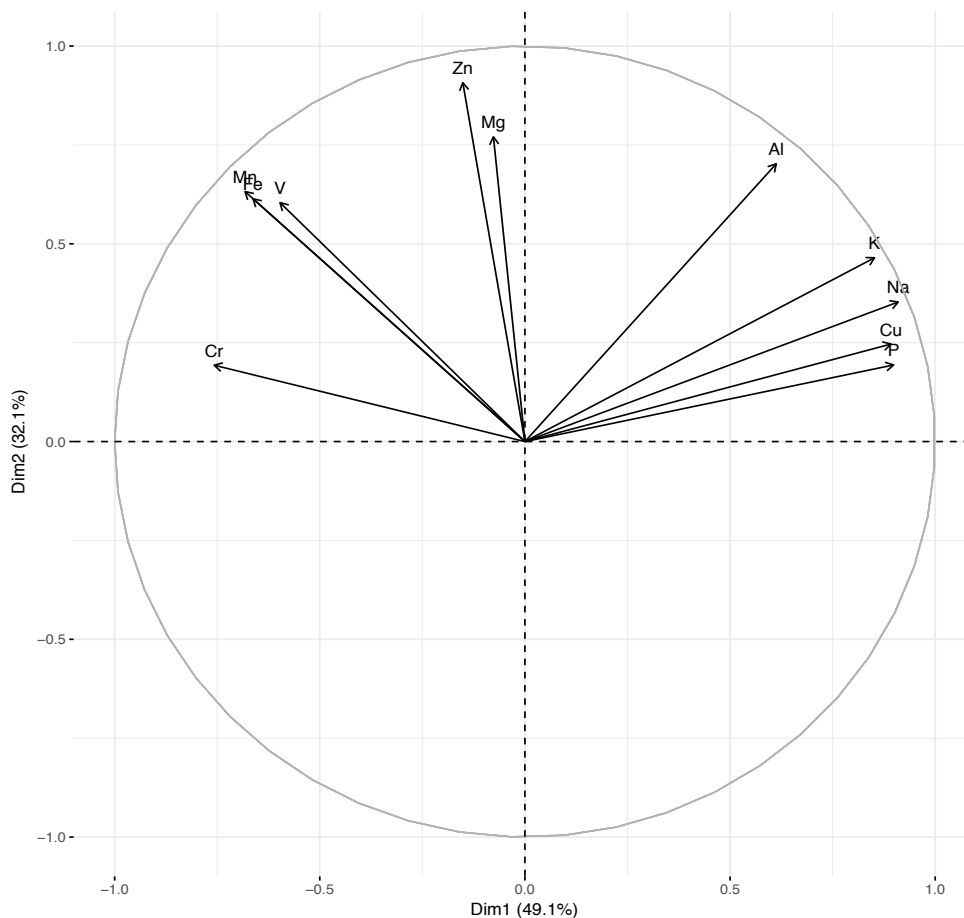
Acid ammonium oxalate treatment, selectively digests iron oxides, amorphous and poorly crystalline minerals. A range of elements are associated with these minerals and mineral coatings. Of those present in the tailings magnetite, calcite, and chlorite-like minerals are most easily attacked by AAO, as will be discussed further in the following chapter. Cu revealed correlations with V, Pb, Cd, Fe, Na, K and P. Mn showed the strongest negative correlation with Cd, Fe, V and Cu (Figure 3.7).

Figure 3.7 PCA diagram – projection of variables on components plane, for the acid ammonium oxalate treatment.



Treatment of the tailings samples with hydrochloric acid resulted in Cu exhibiting significant correlations with a number of elements, but especially with P and Na. V showed the strongest correlation with Mn and Fe (Figure 3.8).

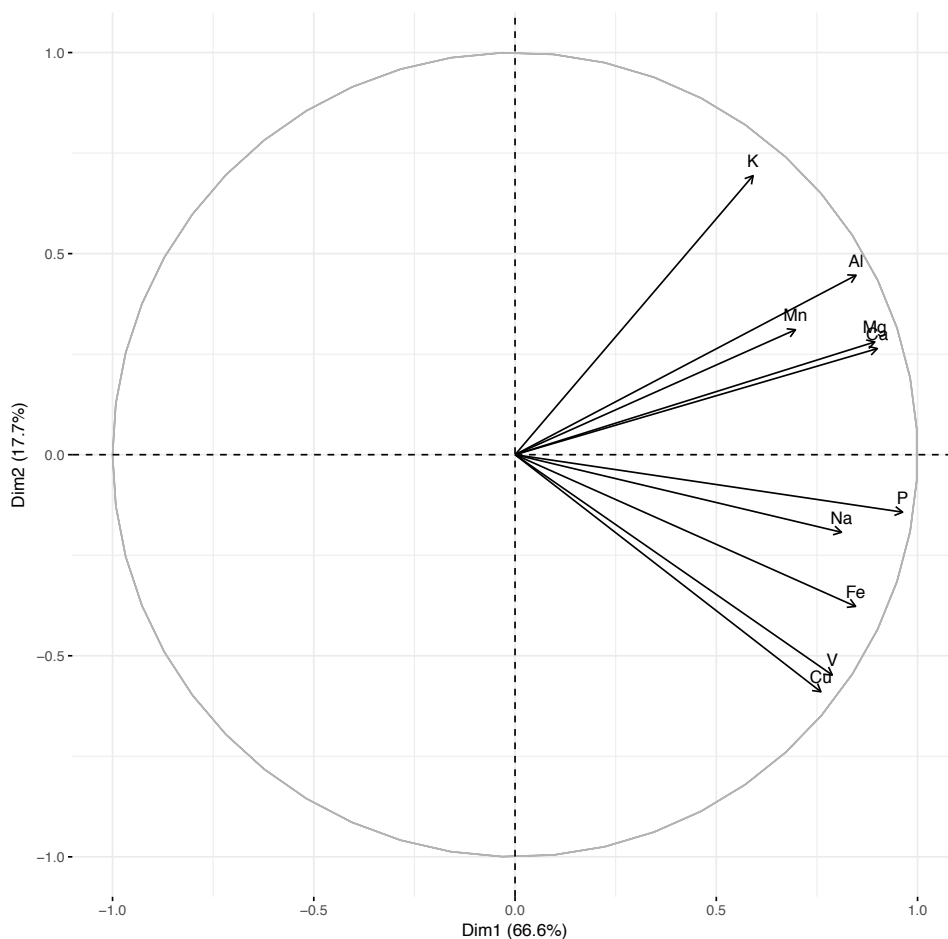
Figure 3.8 PCA diagram – projection of variables on components plane, for the hydrochloric acid treatment.



The PCA diagram for the *aqua regia* treatment showed Cu and V exhibiting strong correlations with Fe, P, and Na. Mg and Ca revealed strong correlations with one and other and also with Al and K (Figure 3.9). The *aqua regia* treatment, which is a more complete digest, indicated a tighter cluster of vectors and therefore less variance. Only 10 of the 17 elements analyzed were above the detection limit for the *aqua regia* extraction, despite all 17 being detectible following acid ammonium oxalate treatment. The elements that were below the detection limit for *aqua regia* included: Cd, Co, Cr, Ni, Pb, and Se.

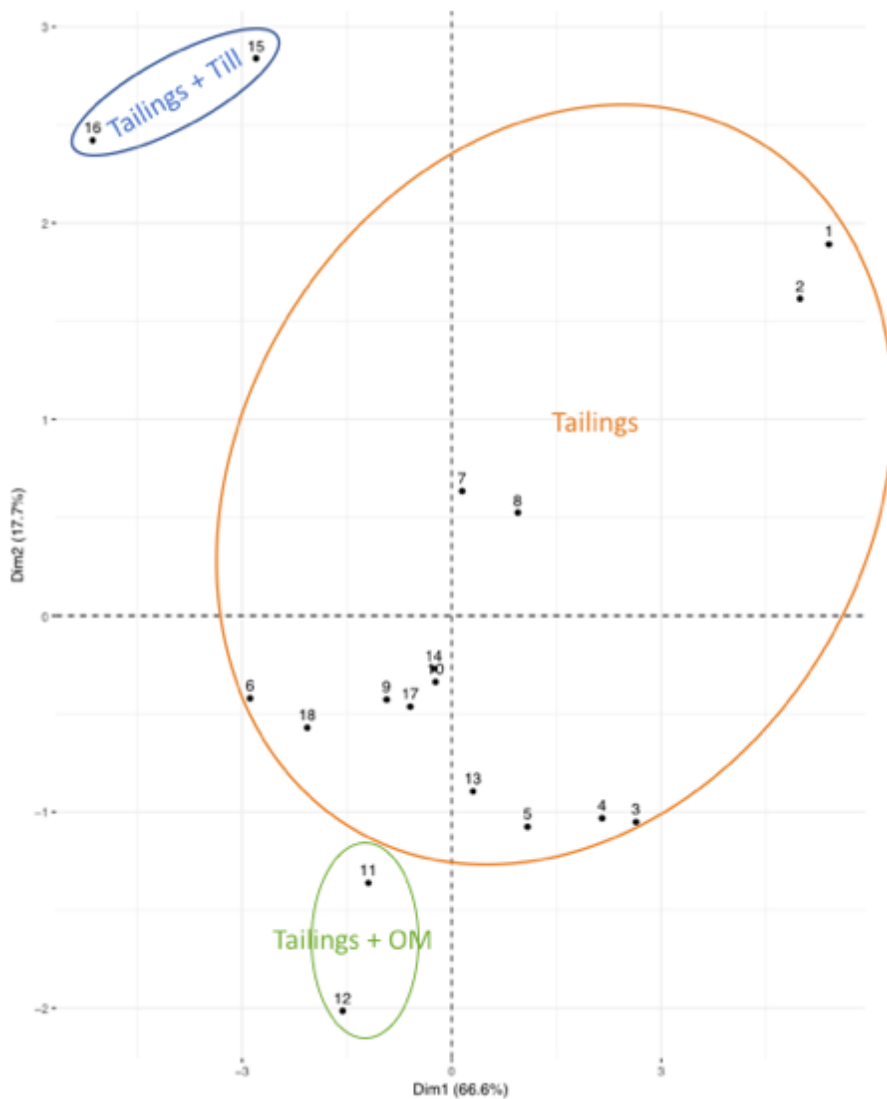
Previous research (Ščančar et al., 2000; Taraškevičius et al., 2013) suggests that *aqua regia* extractions can result in an underestimation of metal contents; the concentration of Cd, Co, Cr and Ni could be under-reported by up to 50%. More recent work on treated sewage sludge reported that the *aqua regia* extractable concentrations of As, Cu, Fe, Hg, Pb and Zn were comparable to total metal content but that Cd, Co and Cr were being underestimated by *aqua regia* treatments by approximately 10% (Santoro et al. 2017). Despite the fact that the ICP-OES results of the *aqua regia* treated samples may have underestimated the amount of Cd, Co, Cr, Ni, it was deemed an appropriate extraction method for recoverable elements because it is the standard method used to determine regulatory limits and thus makes comparisons possible.

Figure 3.9 PCA diagram – projection of variables on components plane, for the *aqua regia* treatment.



The strength of this PCA analysis is its ability to summarize 17 dimensions of chemical data into 2-dimensional space while still accounting for roughly 74%, 82% and 84% of the total variance in the AAO, HCl and *aqua regia* treatments, respectively. Although the combination of the acid treatments and the PCA was not enough to determine the affinity between elements to form secondary minerals, the models showed that different extractions have varying degrees of selectivity for different elements and that there was a clear chemical segregation between materials. This was most noticeable in the *aqua regia* treated samples (Figure 3.10) and suggested that PCA analysis coupled with this extraction method could be a useful way to visualize segregations within the chemical profiles of samples with different material compositions. The scatter plot PCA diagram (Figures 3.10) suggests some spatial segregations from the TSF along Hazeltine Creek to Quesnel Lake, however, the distinction was more marked for the acid ammonium oxalate and hydrochloric acid treatments (Appendix B.1 and B.2).

Figure 3.10 PCA diagram - scatter plot projection of sites on components plane, for the *aqua regia* treatment. (Points 1 and 2 represent Site 1. Odd numbers represent the 0-15cm depth, while even numbers represent the 15-30cm depth).



3.4 Conclusions

This chapter gave a summary of the chemical data of acid treated tailings samples. The reactivity of the tailings materials is a property that must be understood in order to proceed further with restoration efforts and to mitigate future ecosystem health risks of inaction.

The tailings contained significant Cu, V in the bioavailable and mobile fractions. Concentrations of both metals exceeded the CSR guidelines for toxicity to soil invertebrates and plants and have the potential to disrupt ecosystem health structure and functioning. A number of the sites had concentrations of V that surpassed the human health protection for ingested soil. P is an important nutrient for all organisms, however the concentrations of P observed in the tailings were very high and may have adverse effects on the aquatic habitat of Hazeltine Creek and receiving environments. Correlations of the distribution of P relative to other elements revealed that P is likely bound by apatite group minerals.

The PCA analysis of ICP-OES chemical data was able to show a separation in chemical composition between tailings only sites and tailings mixed with till sites this may be useful for informing future sampling strategies and for monitoring purposes.

Chapter 4: The effect of acid treatments on bulk mineralogical properties of the tailings deposited at the Mount Polley spill site.

4.1 Introduction

This chapter examined bulk mineralogical properties of the tailings material in order to determine the potential changes that the minerals might undergo during weathering processes. Fresh, relatively un-weathered tailings samples, collected from the Mount Polley mine spill site, were analyzed using X-Ray Diffraction. Fresh samples were compared to three different acid treated samples to determine the effects on the mineral weathering sequence under simulation experiments.

4.2 Materials and Methods

4.2.1 X-Ray Diffraction

XRD is a relatively common method for identifying crystalline materials (Carrol, 1974). The properties of different minerals are linked to the arrangement of atoms in the crystal lattice structure and therefore, crystalline minerals each have a characteristic ‘fingerprint’ that distinguishes them. Amorphous materials and organic matter lack long-range order and thus cannot be categorized using XRD analysis (Carroll, 1974).

Fresh and acid treated tailings samples were prepared for XRD analysis. From the 14 samples collected per sampling site, a random number generator was used to select a control and a treated sample per site and per acid treatment. The samples were ground using an agate mortar and pestle. Samples were smear mounted on glass plates using anhydrous ethanol. XRD patterns were obtained at a scanning rate of 0.5 seconds using a Bruker D8 Focus X-Ray Diffractometer with $\text{CoK}\alpha$ radiation. Step size was 0.04° over a range of $3\text{-}80^\circ 2\theta$. Phase identification was done using a search/match software by Bruker Diffrac EVA software 3.1 and crystal structure data was obtained from International Centre for Diffraction Database PDF-4 2016 file cards. All the XRD analyses were made at the Department of Earth Ocean and Atmospheric Sciences at the University of British Columbia.

4.3 Results and Discussions

4.3.1 Impact of acid treatments on mineralogy

Visual analysis of the peaks on the XRD patterns and estimation of area under the curve provided the basis for comparison between untreated and acid treated tailings samples (Speakman, 2015). If the shape of a peak lost sharpness and became broader it was assumed that a decrease in mineral crystallinity had occurred. Alternatively, if a peak became sharper and more defined following acid treatment it was assumed that an increase in mineral crystallinity had occurred. If, however, the intensity of the peaks increased, i.e.: the peak height increased, with the sharpness of the peak remaining unchanged, and no additional changes observed to other minerals, it was assumed that the increase in peak height indicated an increase in mineral abundance compared to the other minerals.

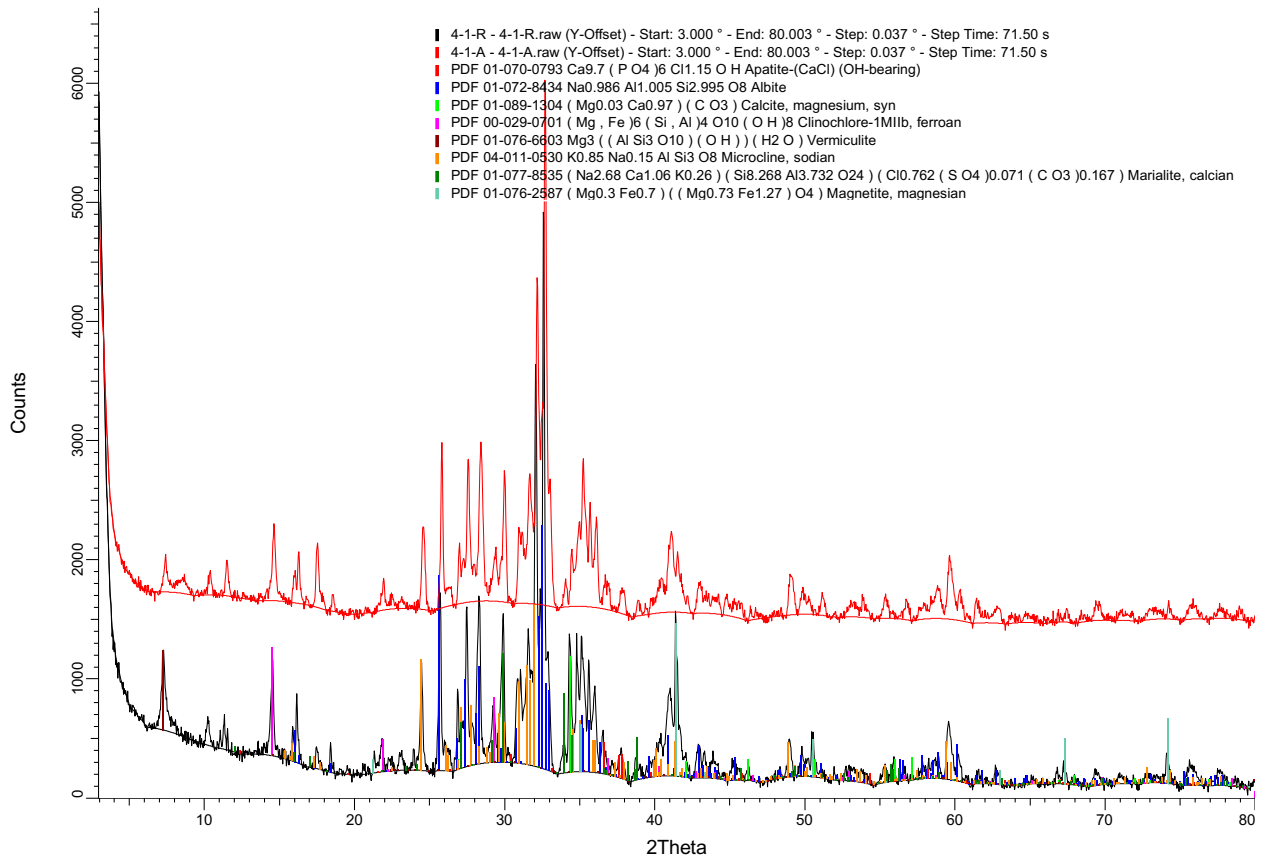
XRD patterns identified the untreated tailings samples as being principally comprised of albite, apatite, calcite, clinocllore, magnetite, microcline and some quartz. Geologic studies of the mine area indicate that the parent material of the site is primarily diorite (Kennedy & Day, 2015). Characteristically this rock is composed of dark-colored amphiboles (especially hornblend), acid plagioclase (oligoclase, andesine), pyroxene and sometimes a small amount of quartz. (Gary et al., 1972).

When tailings samples were treated with acid ammonium oxalate (Figure 4.1), there was a decrease in mineral crystallinity for a number of minerals including calcite, clinocllore, magnetite and in some cases vermiculite. The decrease in mineral crystallinity is observable in the diminished peak height and widening of the peak shoulders.

For convenience, a brief description of the identified minerals is presented. Calcite, CaCO_3 , is a common rock-forming mineral which is easily weathered. Clinocllore, $(\text{Mg}, \text{Fe}^{2+}, \text{Al})_3(\text{Si}, \text{Al})_2\text{O}_5(\text{OH})_4$, is a greenish mineral of the chlorite group that can contain significant Fe^{2+} . Magnetite, $(\text{Fe}, \text{Mg})\text{Fe}_2\text{O}_4$, is part of the spinel group of minerals and can contain varying amounts of titanium oxide and in igneous rock formations, it can be present as a primary mineral or as a secondary alteration product. Vermiculite minerals, $(\text{Mg}, \text{Fe}, \text{Al})_3(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, are micaceous clay minerals that are closely related to chlorite and montmorillonite.

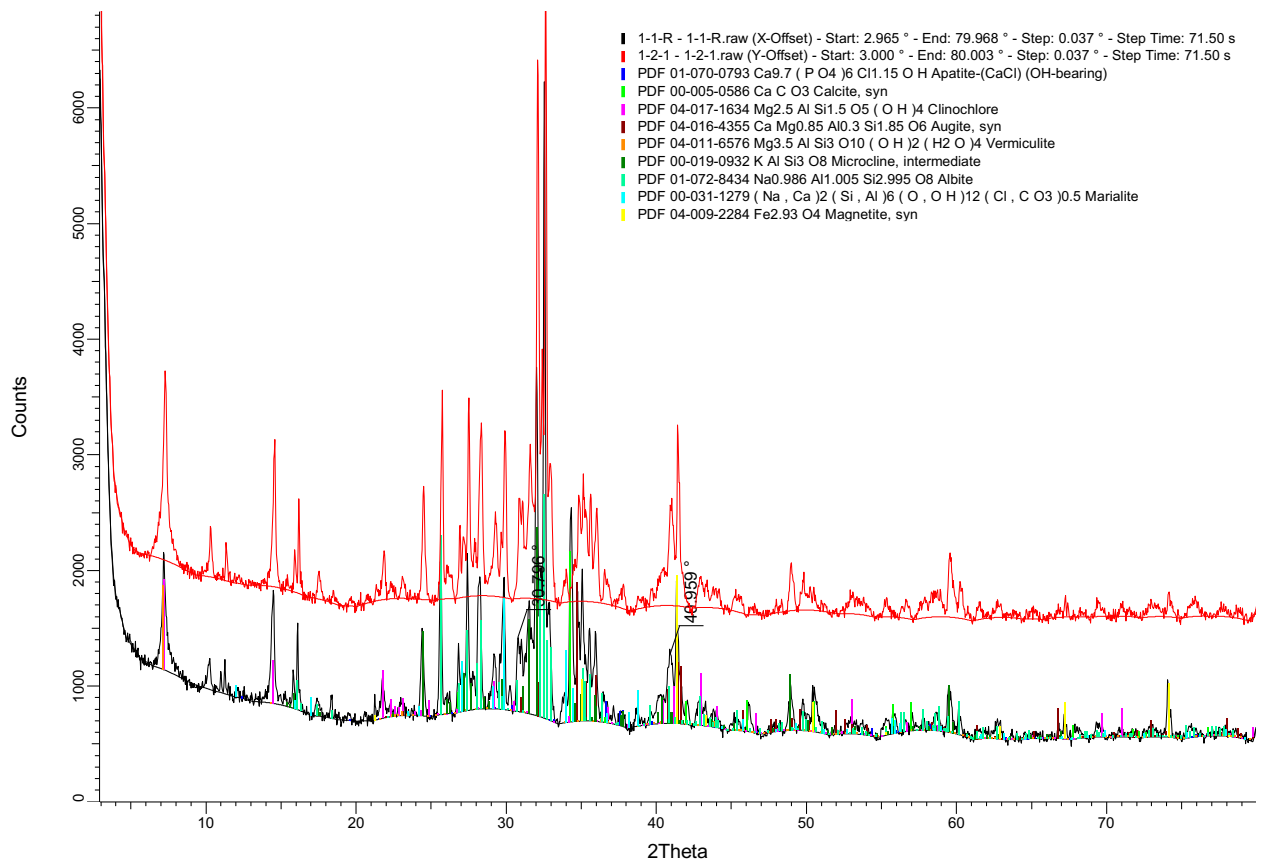
Although, acid ammonium oxalate attacks the amorphous coatings of minerals the surfaces undergo a continuous conversion from amorphous to crystalline and back to amorphous. XRD pattern analysis showed little evidence that upon treatment with acid ammonium oxalate the minerals in the tailings samples become increasingly crystalline.

Figure 4.1 XRD pattern Site 4 (0-15cm) untreated sample (black) compared to Acid ammonium oxalate treated sample (red).



When tailings samples were treated with hydrochloric acid there was a decrease in the amount of mineral calcite. This was indicated by a decrease in peak height (Figure 4.2). For a few samples that contained clinocllore and/or vermiculite, treatment with hydrochloric acid resulted in greater crystallinity of both the aforementioned minerals. Greater crystallinity was revealed through sharper peaks and a narrowing of the shoulders associated with the peaks of those minerals (Figure 4.2).

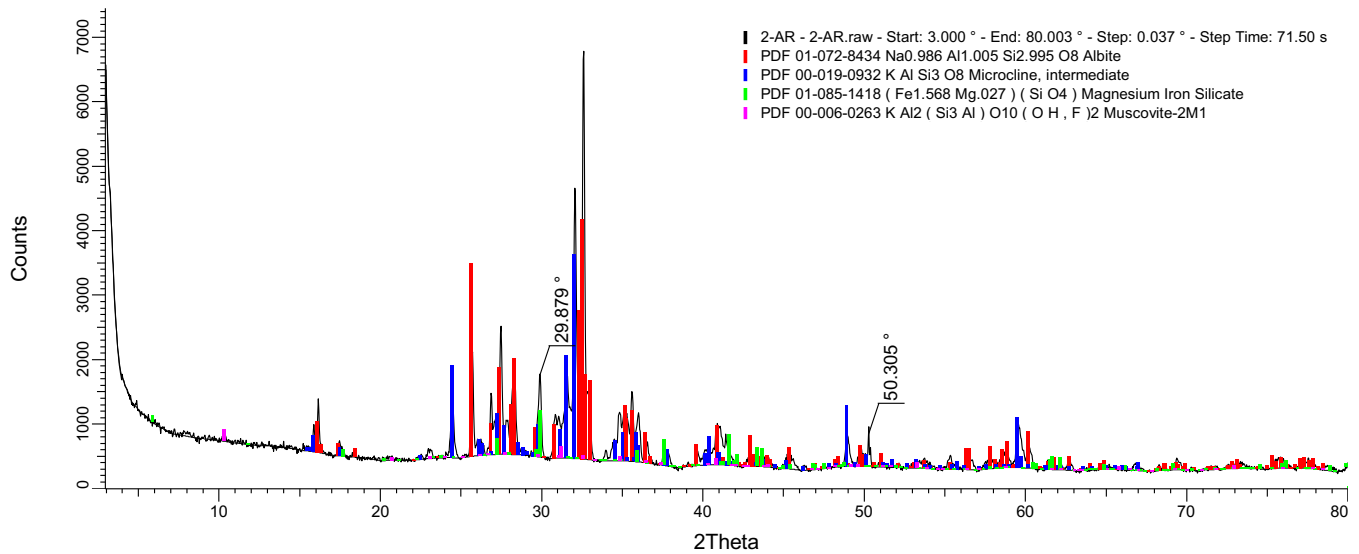
Figure 4.2 XRD pattern Site 1 (0-15cm) untreated sample (black) compared to hydrochloric acid treated sample (red).



Albite, microcline, muscovite and quartz, present in the fresh tailings samples, are the minerals that remained intact following *aqua regia* treatment (Figure 4.3). The other minerals present in the untreated samples were destroyed and the elements associated with them are those that were observed in solution during ICP analysis. The persistent minerals are those that are the

most highly resistant to weathering processes and that are the least likely to undergo alterations when exposed to earth's surface conditions. Their crystalline structure was highly stable compared to the pyroxene, amphiboles and plagioclase feldspars that were observed more commonly in the XRD patterns of the fresh tailings.

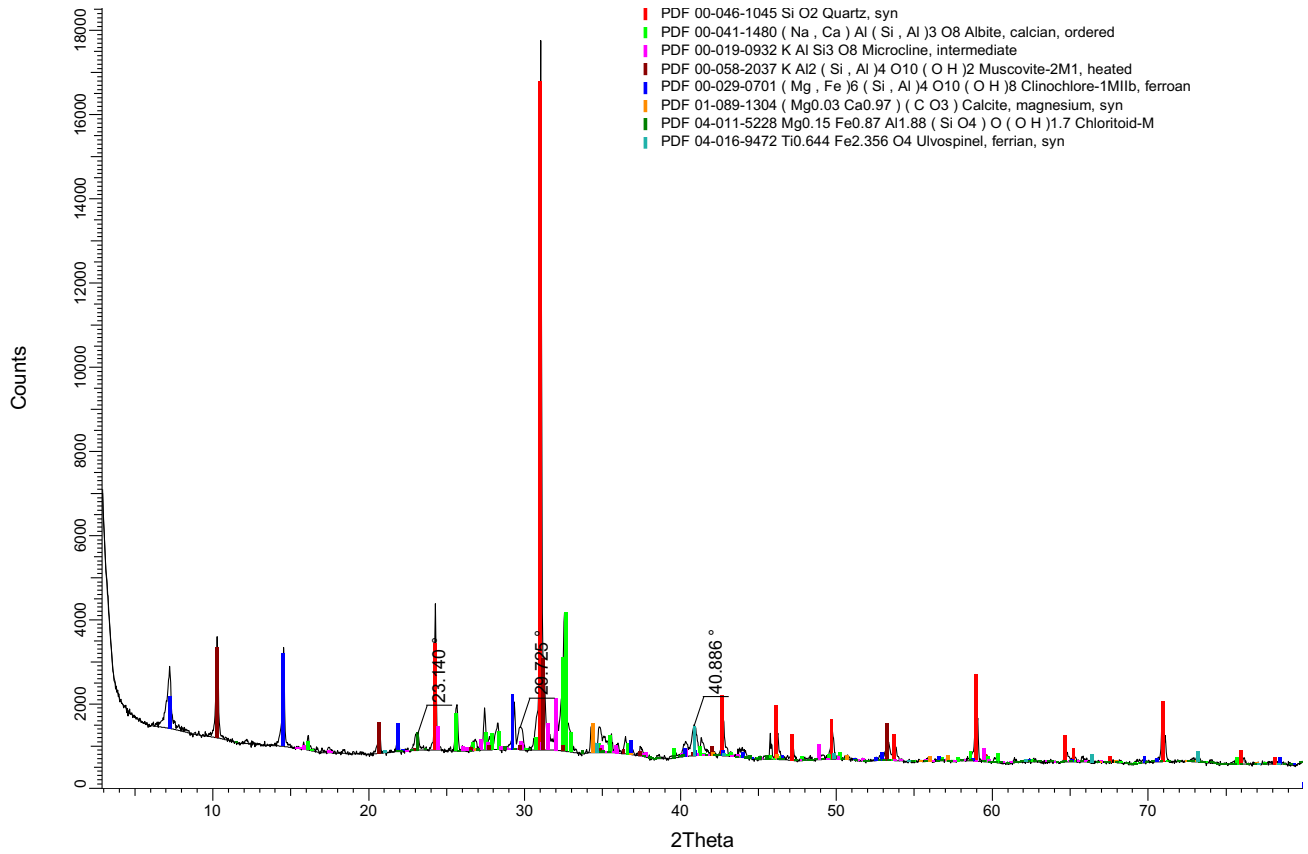
Figure 4.3 XRD pattern Site 2 *aqua regia* treated sample.



4.3.2 Mineralogical comparisons between tailings and till

Restoration efforts had begun at Site 8 prior to the sampling event in the summer of 2016. Some tailings had been removed from the site, and the remaining tailings had been incorporated with till material. XRD scans of the raw material indicated that, unlike the other sites where tailings were the dominant material, quartz minerals were prevalent in samples containing till. XRD pattern analysis also identified albite, muscovite and clinochlore as having high crystallinity (Figure 4.4). The tailings and till mixture XRD patterns illustrated a simpler composition with fewer minerals present. In contrast, the tailings dominated samples were more heterogeneous and minerals showed variable susceptibility to weathering.

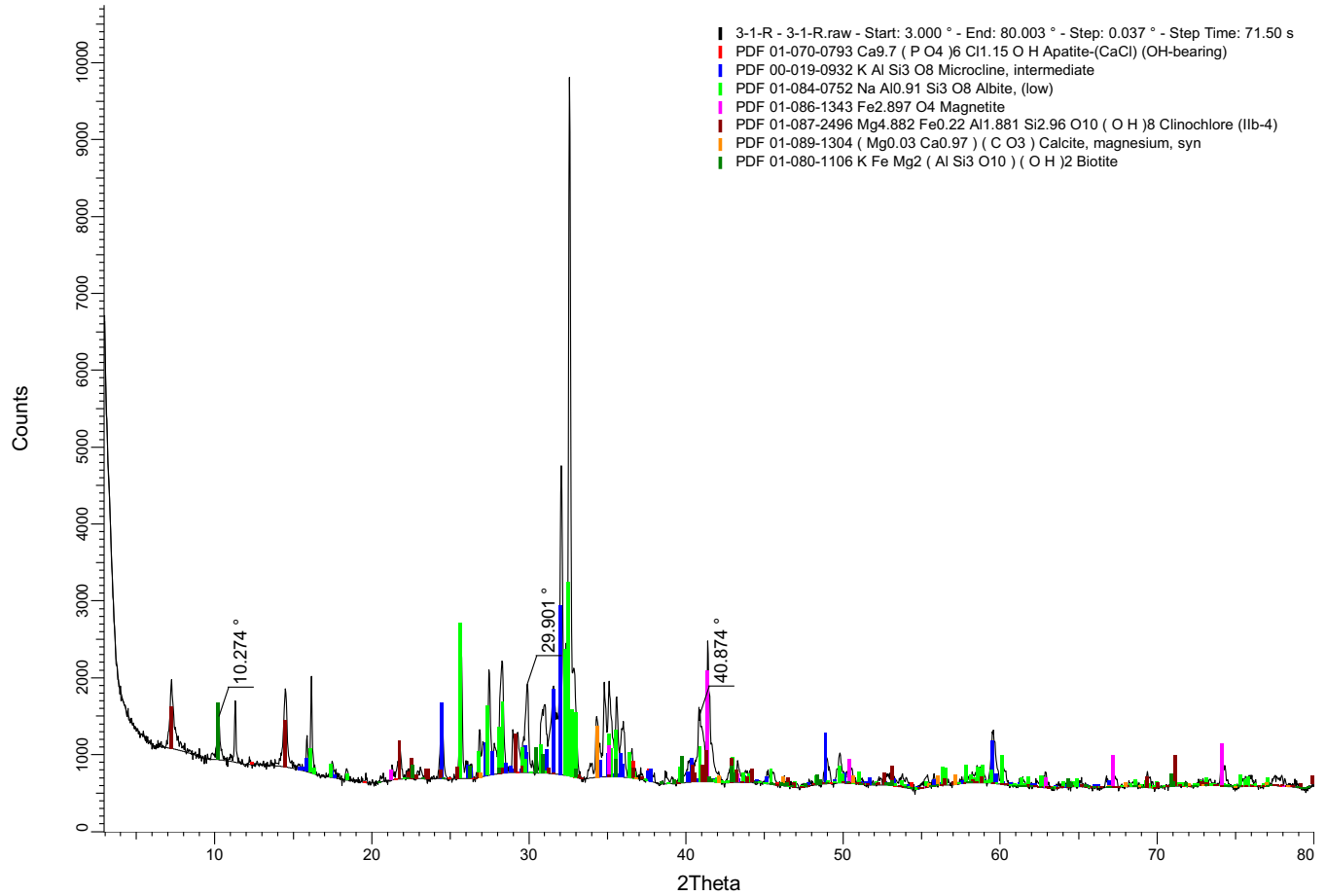
Figure 4.4 XRD pattern untreated Site 8 (0-15cm).



In general, the minerals present in the tailing and till mixture included more stable felsic minerals that are not as commonly associated with heavy metals (Parker, 1967). The tailings and till material was less reactive and less susceptible to alterations caused by acid treatment

Raw tailings samples contained very little quartz. Calcite, clinochlore, magnetite, microcline, albite and apatite were commonly observed as is shown in the illustrative example from Site 3 (Figure 4.5).

Figure 4.5 XRD pattern untreated Site 3 (0-15cm).



4.3.3 Challenge of identifying multiple minerals

Conducting XRD analysis on tailings samples was not straightforward because of the range of structural and chemical compositions of the minerals present. XRD cannot quantitatively assess mineral abundance and in addition, it is difficult to identify poorly crystalline minerals due to their typically broad, low intensity diffraction peaks. Minerals of minor elements can also yield the same characteristically low-intensity peaks that commonly overlap with high-intensity silica peaks

thereby making identification challenging. For some minerals that were found in the tailings, such as calcite and dolomite, overlap of the XRD peaks is typically not a problem, however, others like albite, anorthite, cristobalite, kaolinite, muscovite and orthoclase are known to have interfering peaks with quartz (Prickard et al., 1985)

As mentioned in the previous chapter, field observations, noted numerous algal blooms along the length of Hazeltine Creek during the time of sampling in June 2016. It was hypothesized that the blooms were related to an abundance of phosphorus either entering the creek from forest organic matter runoff or from the solubilisation of tailings material. IPC analysis confirmed high phosphorus concentrations in the tailings samples. Initial investigation of XRD patterns, which were performed using the Eva program's general search engine, did not reveal evidence of phosphate mineralogy. This was not surprising as P mineral content in soils is generally too low for direct identification by XRD (Lindsay & Vlek, 1977). However, because this finding was inconsistent with the chemical data, a more specific search, employing specific machine settings to detect lower concentrations for phosphate bearing minerals was performed. In doing so, apatite, and/or apatite group minerals were observed in nearly all the untreated tailings samples.

4.4 Conclusions

Weathering simulation experiments were conducted in the laboratory to describe the mineralogical alteration of the tailings from acid treatment. Fresh samples, collected in June 2016 are considered unweathered as the mined material has not been exposed to oxidizing conditions for long enough to have been significantly altered. XRD scans of the raw material supports findings by SRK Consulting regarding the mineral composition of the tailings material.

Studies that have attempted to identify the mineralogy of soil have found that XRD is incapable of differentiating minor minerals in samples (Singh & Agrawal, 2012). Researchers attributed this to the fact that minerals present in minor concentrations often yield diffraction patterns with broad low-intensity peaks. It is presumed that a similar type of concealment may be occurring in the tailings samples, in particular with regards to sulphide minerals. Because of the mineral heterogeneity of the tailings samples minor minerals are likely being masked by the more dominant minerals in the tailings.

Although the major constituent minerals in the tailings resist rapid phase change, others, present to a lesser degree, may be more susceptible to weathering. Chemical and biological weathering processes can release metals without significantly altering the crystalline structure of highly resistant minerals. Calcite and magnetite found in raw tailings samples were significantly altered following all three acid treatments. While there may not have been dramatic changes to the mineral composition of the tailings, the release of metals and nutrients from amorphous surfaces and minor constituent minerals can still be significant and have an impact on long-term ecosystem health.

The results do show that even in the relatively young tailings sediments, there were indications of variable susceptibility to weathering. It must, however, be kept in focus that the extraction methods used were merely simulations of the weathering processes.

Chapter 5: Conclusions and Recommendations

The susceptibility of the spilled Mount Polley tailings material to weathering processes must be understood to predict the reactivity of the tailings material in the riparian environment. This preliminary work set the stage for the longer-term dynamics of mineral weathering, nutrient cycling and the release of potentially toxic elements as the tailings interact with different naturally occurring acids in the surrounding weathering environment.

Chemical weathering is significantly controlled by pH, redox potential, clay and organic matter. The current alkaline condition of the tailings may be controlling the release of trace metals as metal-immobilization increases with pH (Kotuby-Amacher & Gambrell, 1988), however, the material will become increasingly acidic as weathering proceeds and thus measures should be taken to prevent uncontrolled metal release. The incorporation of organic matter, and in particular humic matter, is recommended as it is one of the primary immobilizing agents for trace metals (Gerritse and van Driel, 1984; Levi-Minzi et al., 1976) and the tailings has been shown to be lacking in it. Organic matter will also improve aeration and porosity, and reduce compaction within the tailings deposition layer. In addition, it will provide necessary nitrogen for plant growth. Stable, soluble organo-metal complexes may increase the mobility of metals, thus water quality in Hazeltine Creek and Quesnel Lake should continue to be monitored as should benthic zones (Jansen et al., 2004; Wuana, and Okiemen, 2011.) Long-term monitoring of resident fish and migratory fish populations is recommended as the impacts of the tailings storage facility failure may not be observed except in future generations

Revegetation strategies including nitrogen fixing species, like alder that has been planted, as well as plants that are unlikely to be grazed heavily by browsing ungulates are encouraged so as to improve the growing medium and reduce the chances of foraging animals ingesting plant tissues with high concentrations of trace metals. The accumulation of trace metals in plant shoot tissues is still not well understood under field conditions, and tends to differ substantially between and within vegetative species (Huang & Cunningham, 1996; McGrath et al., 2002).

Although site prep (re-contouring, mixing, hilling) will improve the chances of successful regrowth, as regrowth and microbial populations re-inhabit the landscape, oxalic acid will be ubiquitous in the growing medium. Acid treatment simulations revealed that significant copper and vanadium are associated with oxalate soluble fractions. As always, restoration work requires

understanding the contribution and balance of physical, chemical and biological processes. Although this research did not include simulations of the microbiological contribution to the weathering processes, it was revealed that chemical processes are capable of altering mineral assemblages and solubilizing trace metals and nutrients. Raw tailings samples weathered under simulation experiments in the laboratory, experienced moderate weathering of chlorite group minerals. Major constituent feldspar group minerals, quartz and muscovite, resisted rapid phase changes despite acid treatment. Calcite and magnetite minerals were significantly altered by all three extraction methods. The alkaline pH of the relatively young tailings deposits along Hazeltine Creek is buffered by the abundance of calcite minerals. The rate of calcite dissolution exceeds that of most other minerals present in the tailings and as it is depleted the material will progressively become more acidic.

Phosphorus is important for successful vegetation growth; however, proper management is encouraged because excess phosphorus may be transported out of the terrestrial system. The impact that it has on aquatic systems can be deleterious. If fertilization is deemed a necessary component of the revegetation strategy of the Hazeltine Creek channel, a non-phosphorus, or low phosphorus fertilizer that is high in organic matter and available nitrogen is recommended.

Multivariate analysis of the chemical data provided some preliminary insights into the affinity of elements in mineral form, in the future, PCA descriptive statistics could be coupled with elemental concentrations obtained from energy dispersive X-ray fluorescence (EDXRF). This combination of techniques has enabled other researchers to predict the mineralogical composition of soil samples from element concentrations (Singh & Agrawal, 2012). PCA was effective in this study for visualising the relatedness of like materials (tailings vs tailings + till); it validated the hypothesis that different materials would exhibit different chemical profiles and that there was a relationship between proximity to the TSF and chemical composition. This may prove useful for informing future sampling and on the ground monitoring.

This exploratory research showed that the tailings sediments have variable susceptibility to weathering but it should be considered that these were strictly simulation experiments that are not entirely reflective of the processes that will occur over the long-term in the field, where biological, chemical and physical processes interact to influence mineral alteration.

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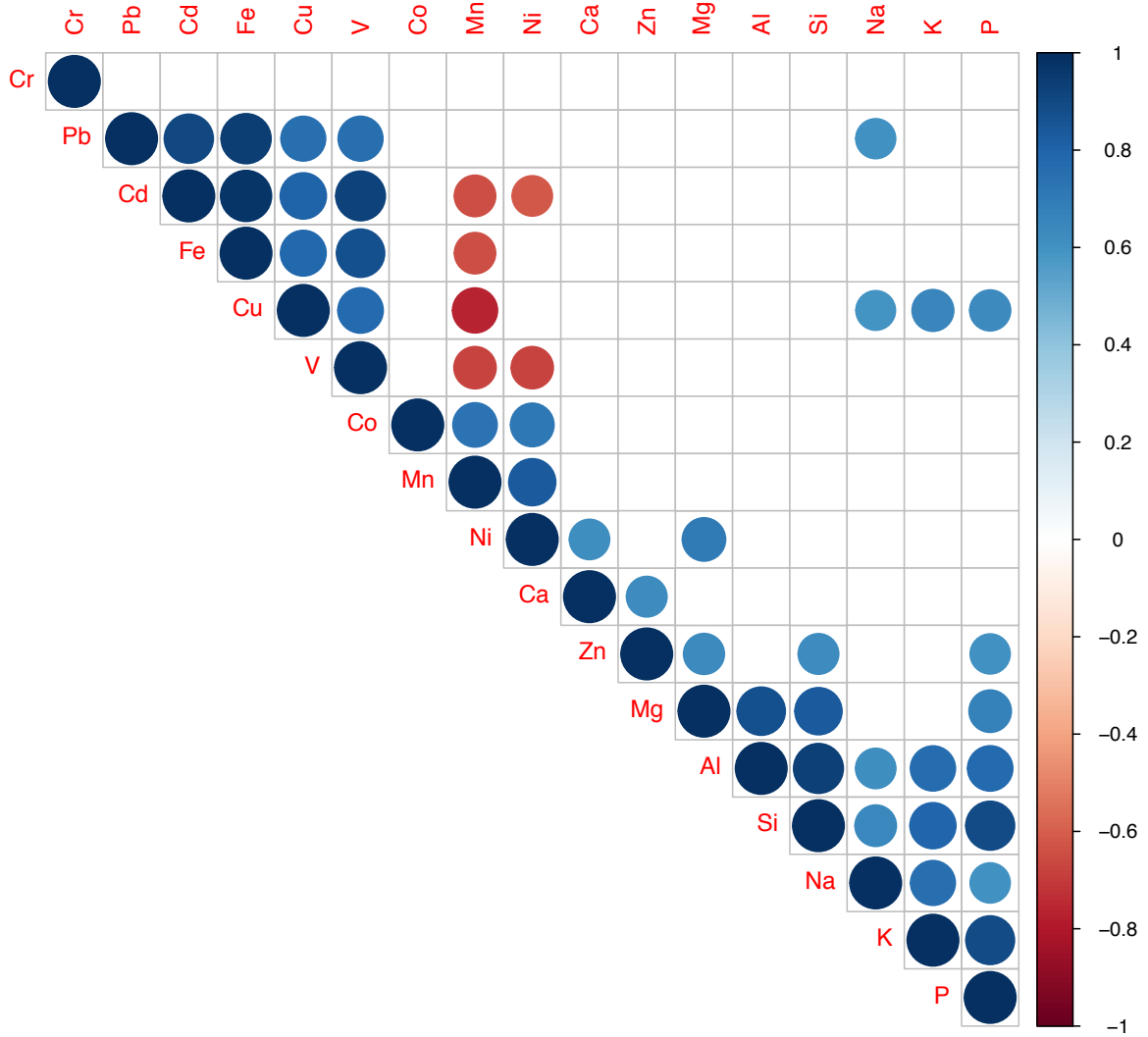
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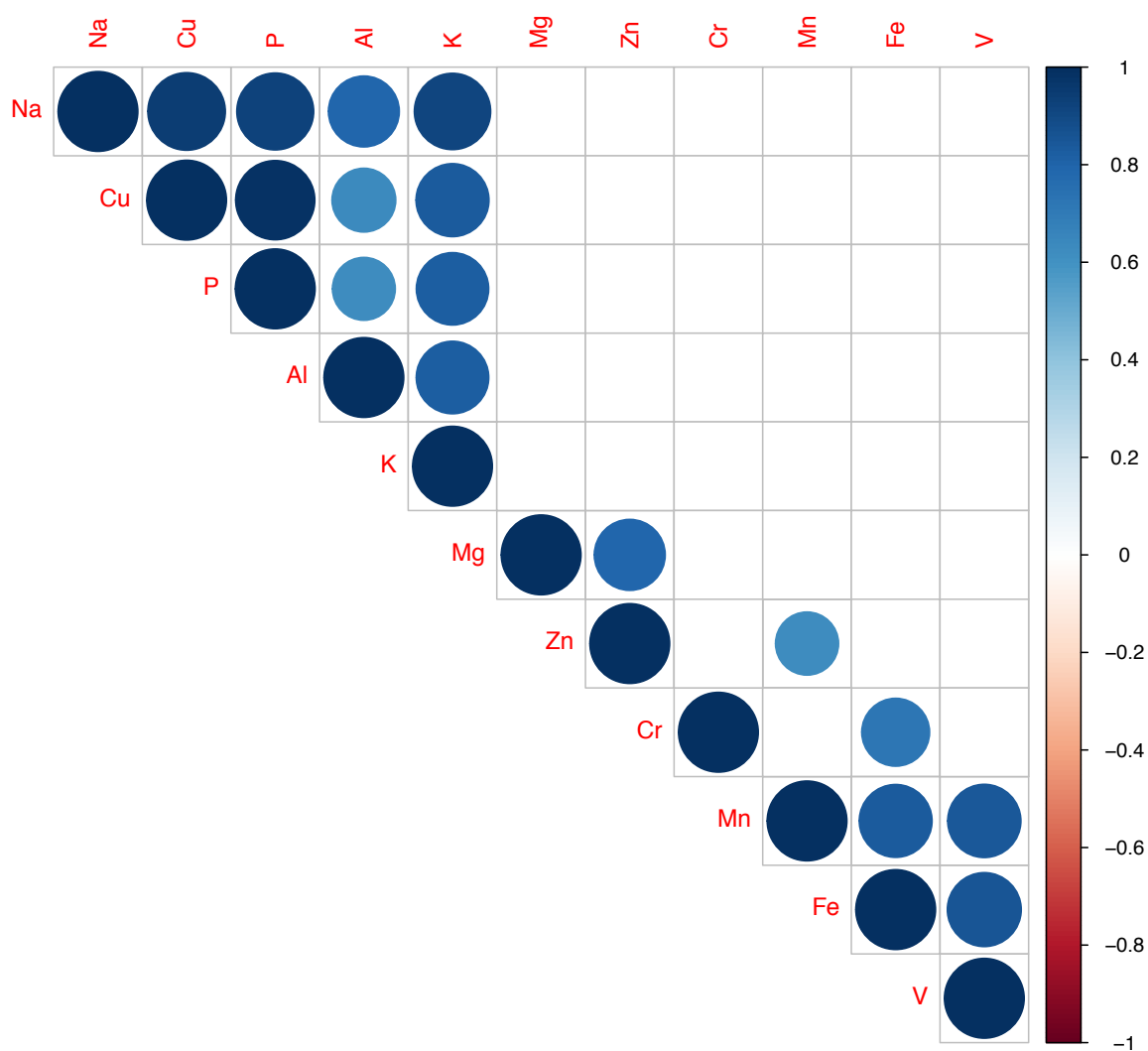
Appendix A

Elemental Correlations

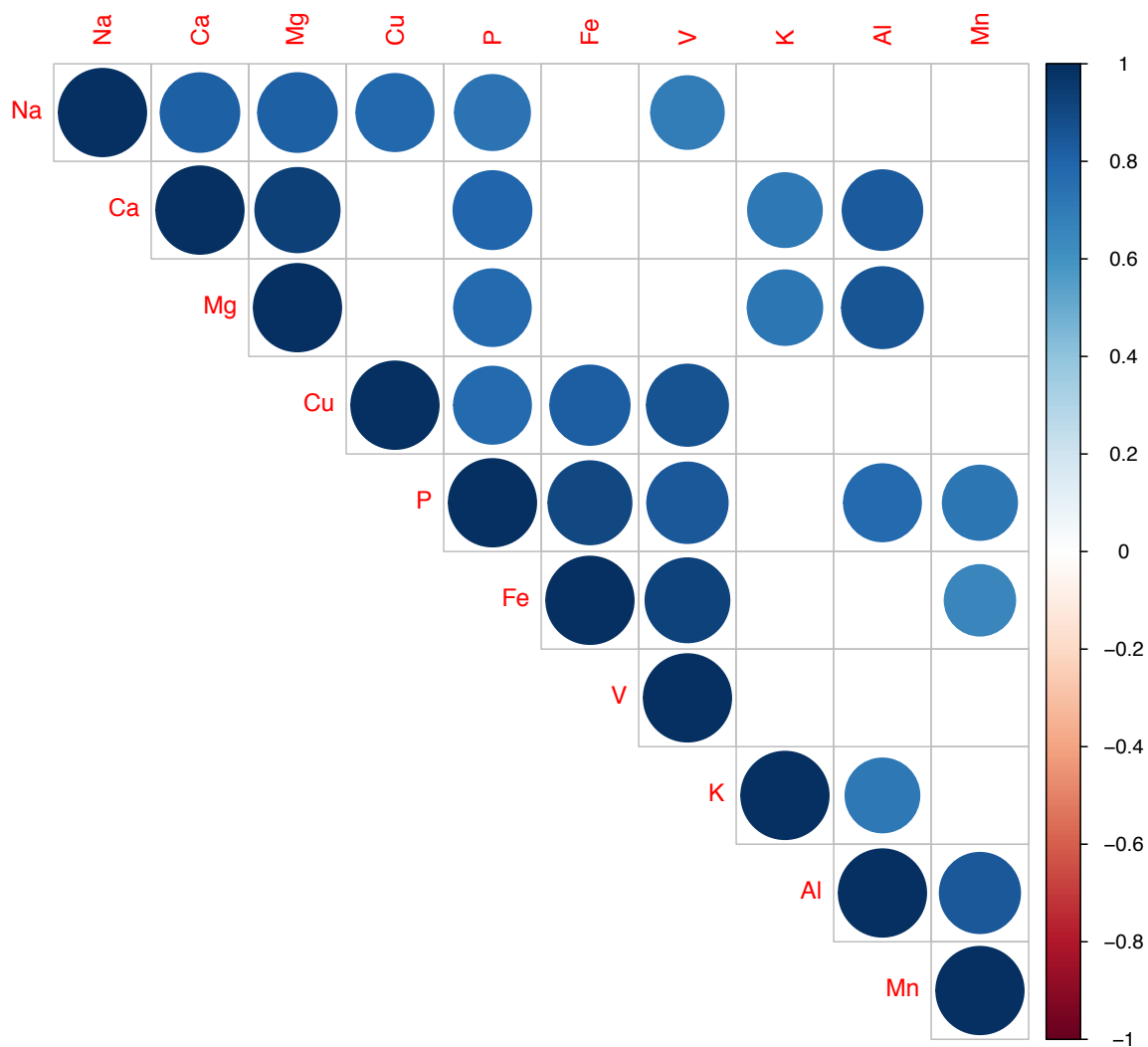
A.1 Acid Ammonium Oxalate Treatment ($p = 0.01$)



A.2 Hydrochloric Acid Treatment ($p = 0.01$)



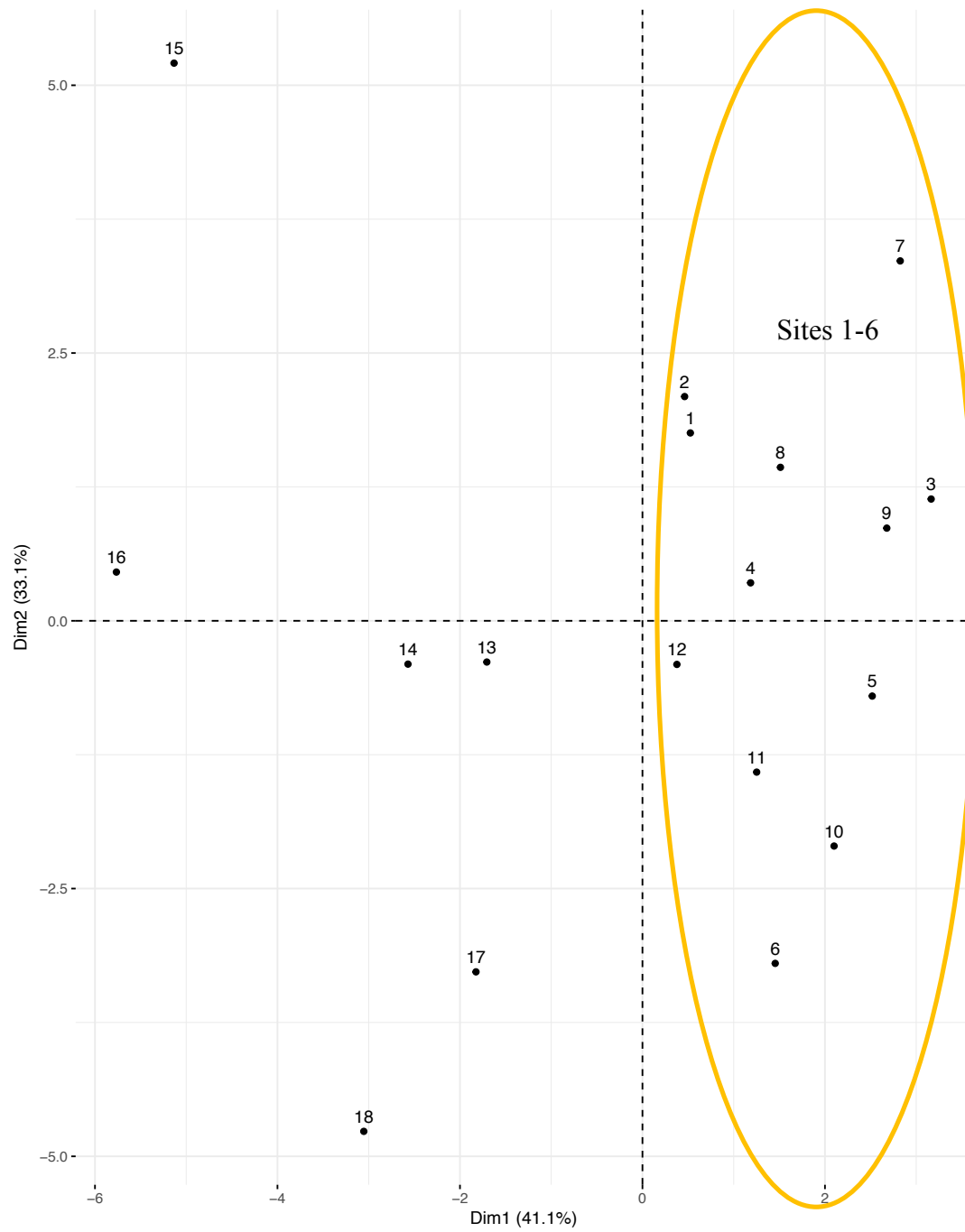
A.3 *Aqua Regia* Treatment ($p = 0.01$)



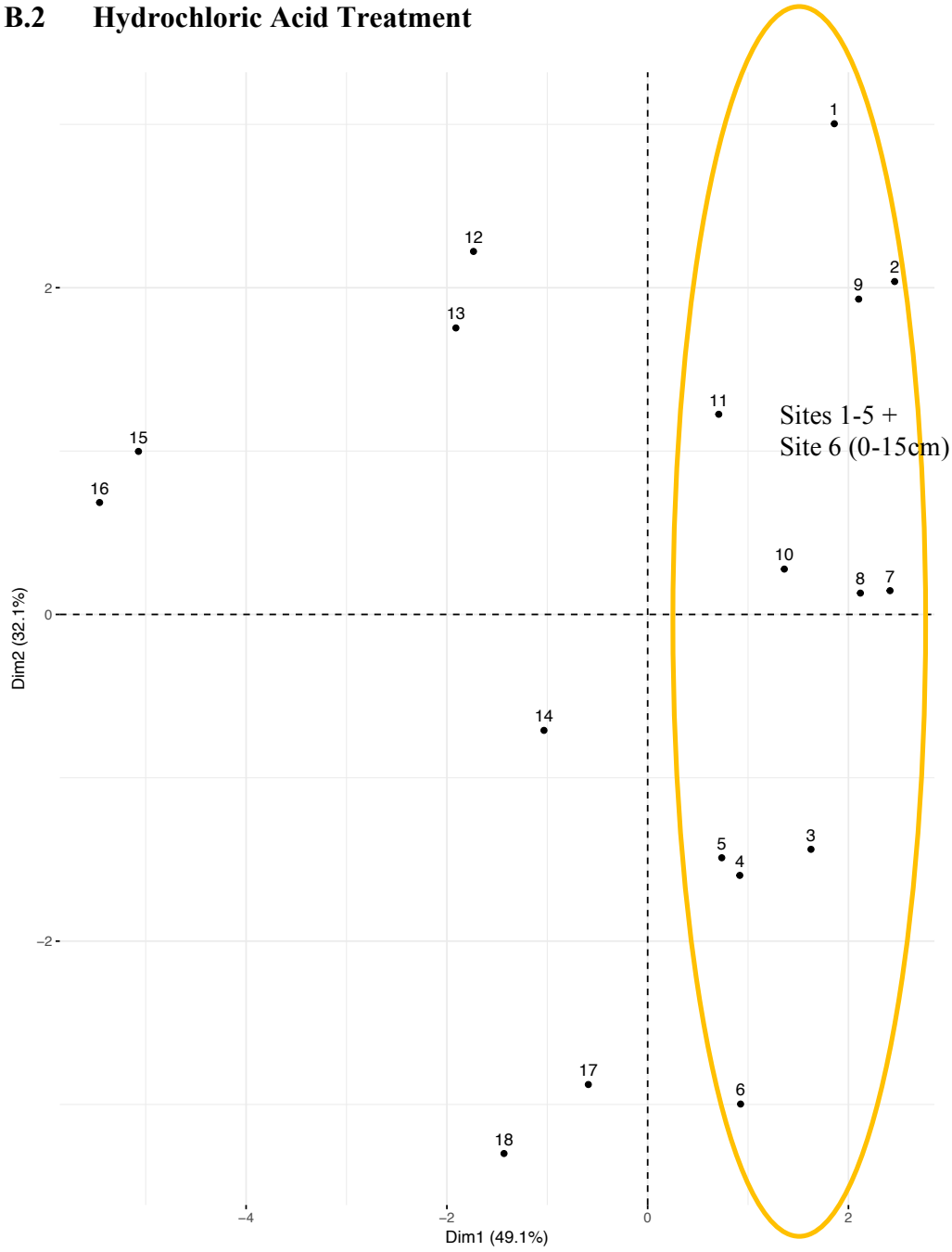
Appendix B

PCA Scatter Plot Diagrams

B.1 Acid Ammonium Oxalate Treatment



B.2 Hydrochloric Acid Treatment

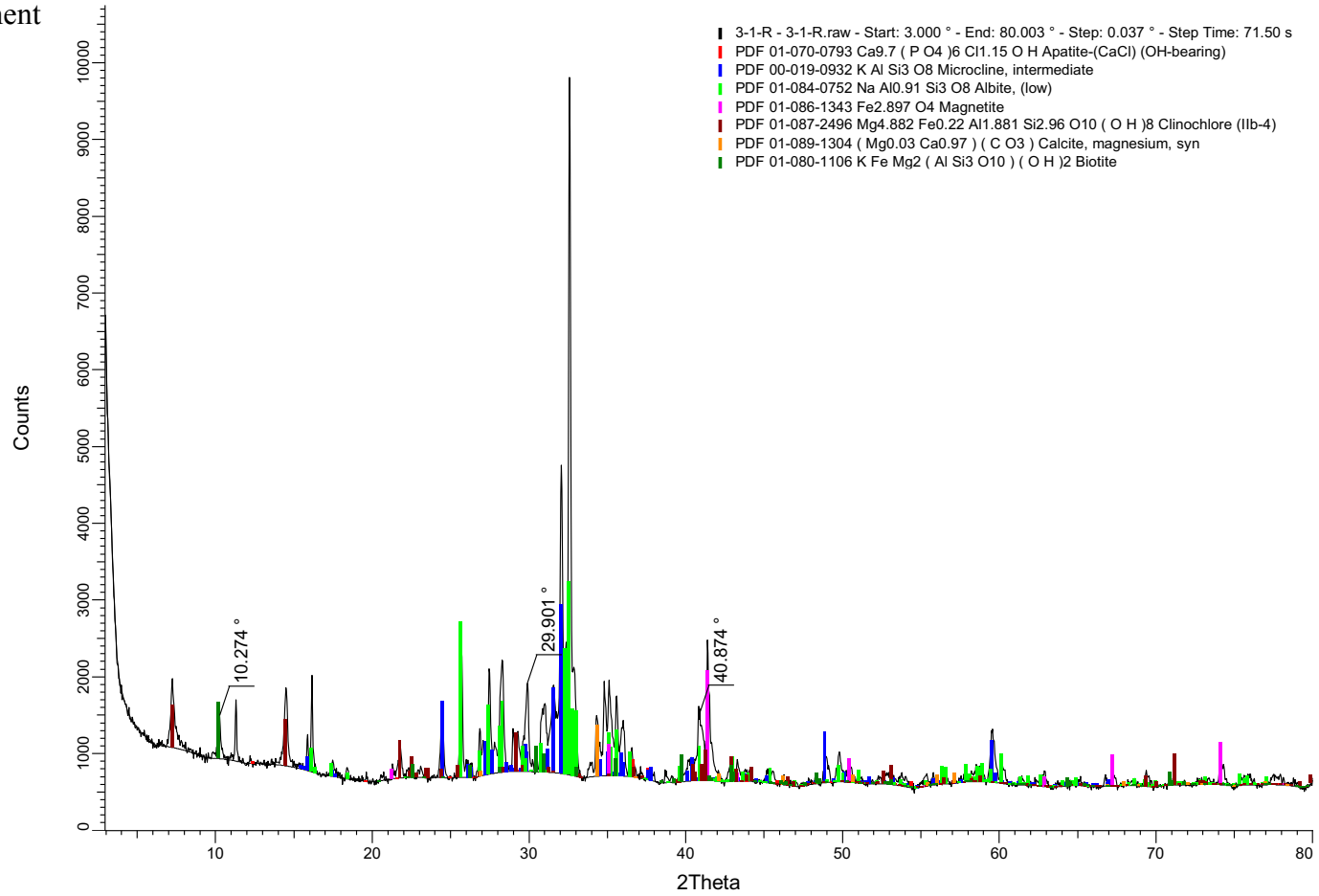


Appendix C

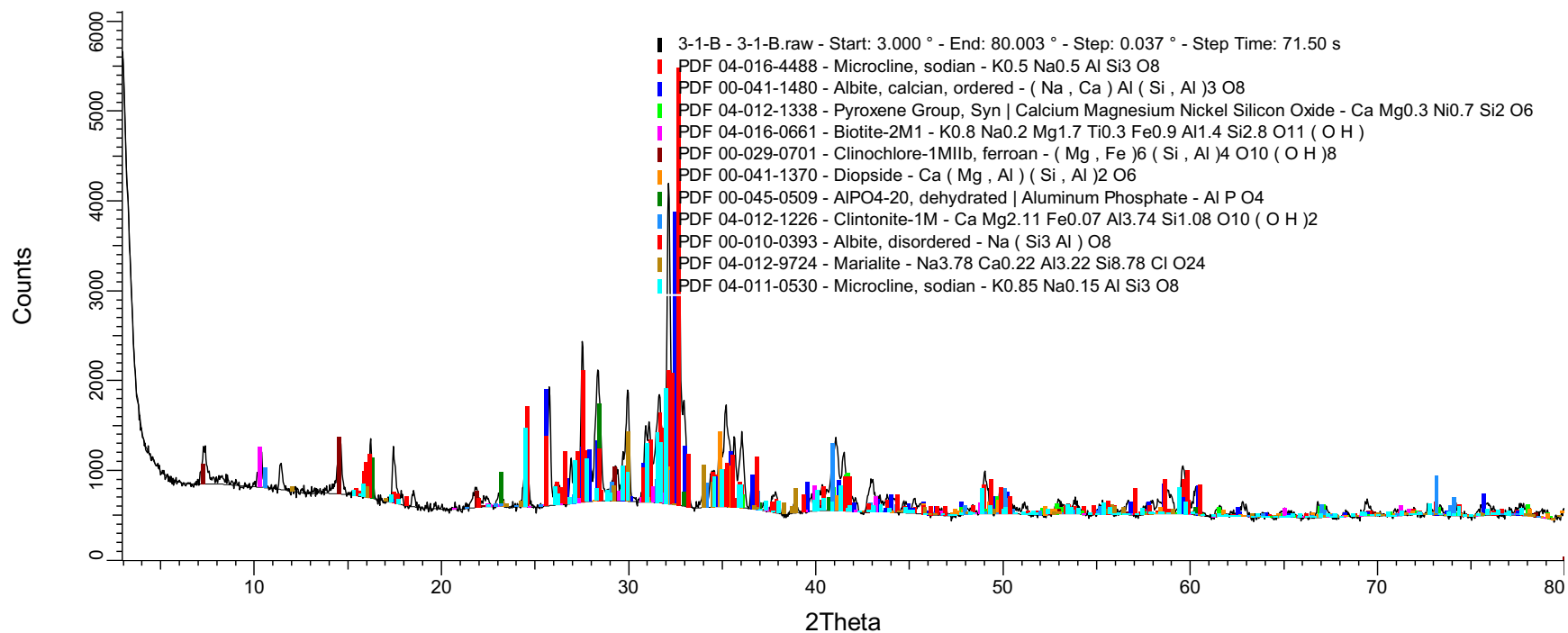
XRD Patterns

C.1 Site 3 (Polley Plug area)

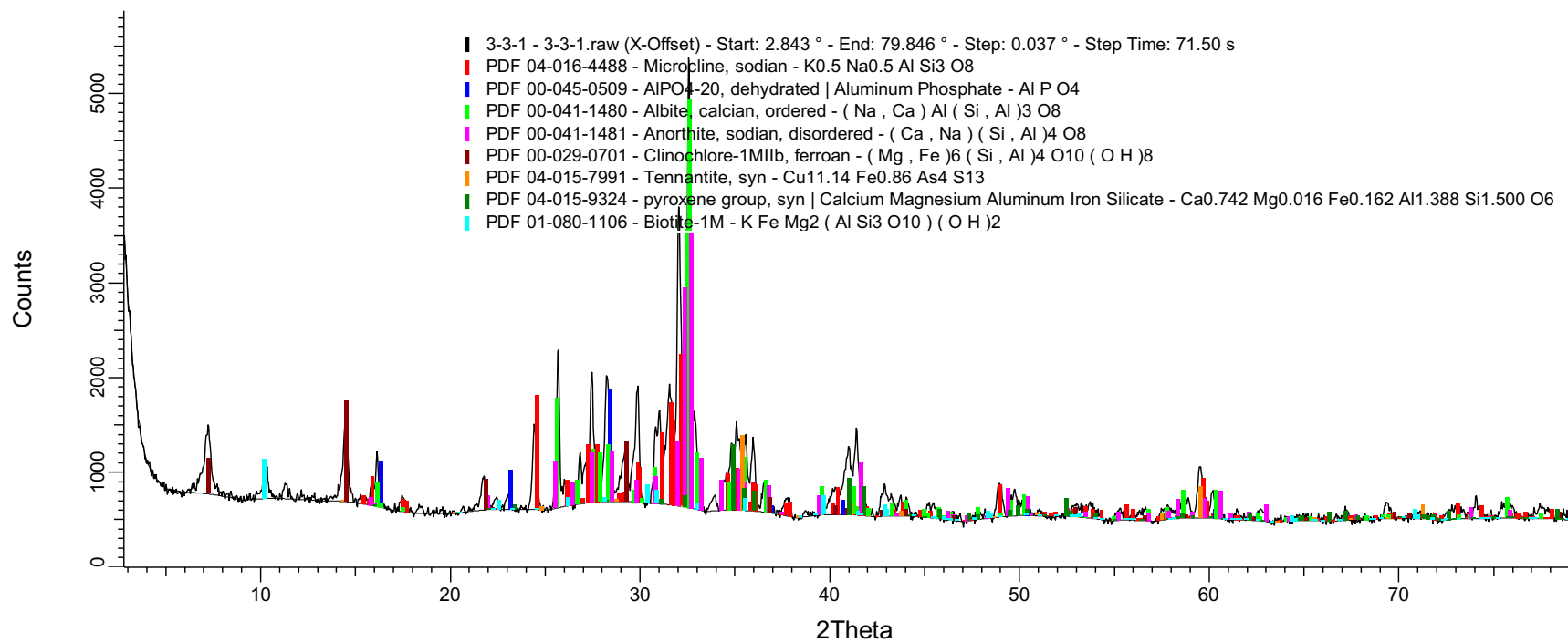
- No Treatment



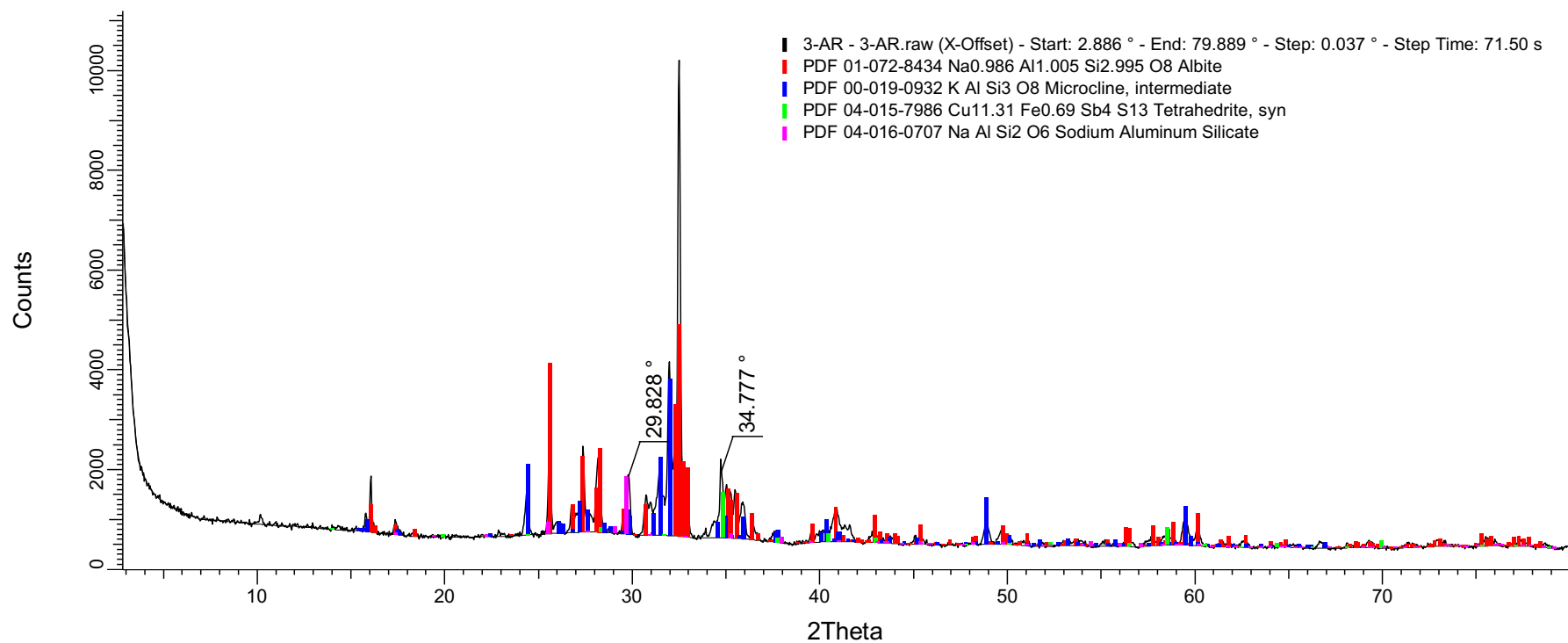
- Acid Ammonium Oxalate Treatment



- Hydrochloric Acid Treatment

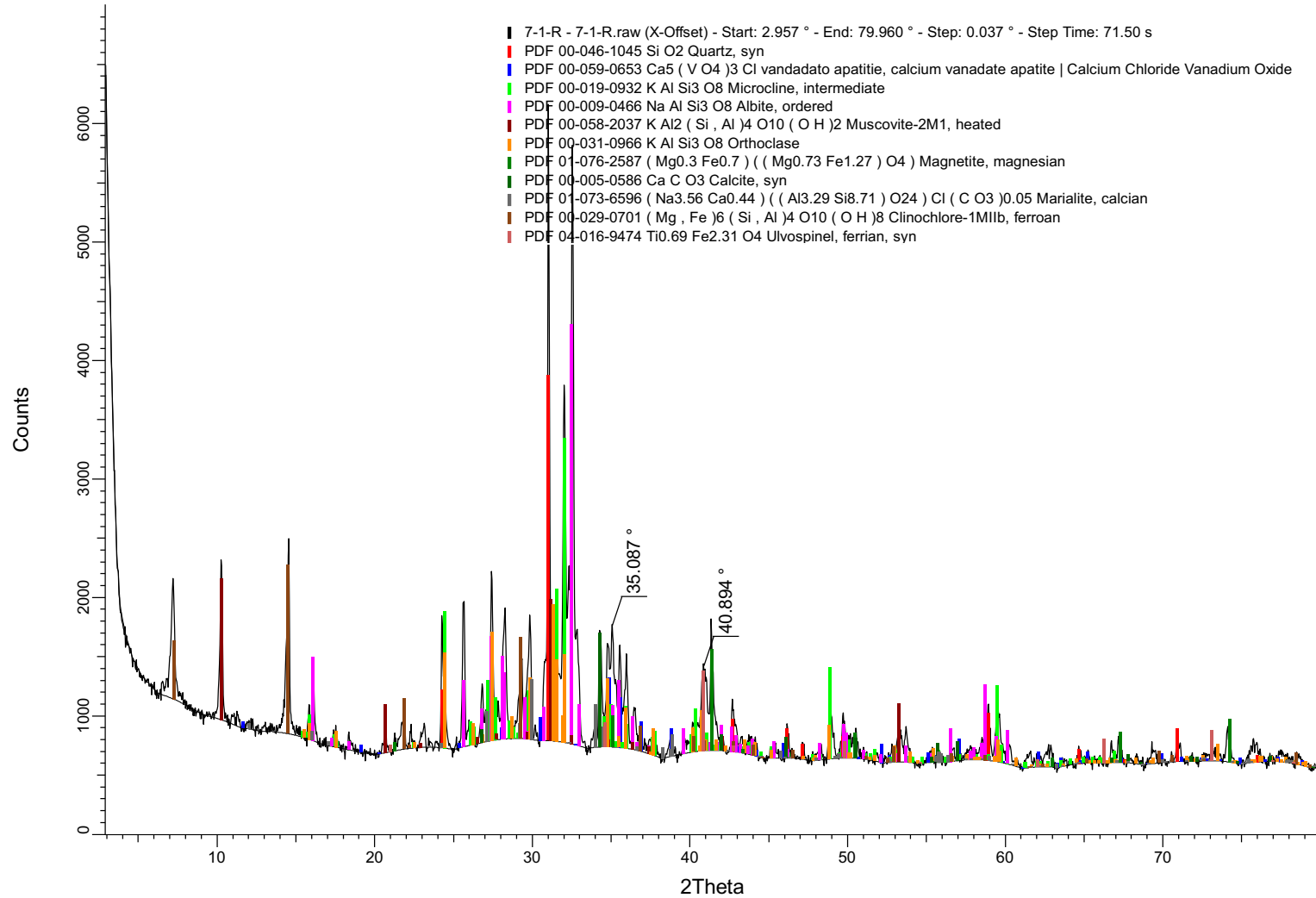


- *Aqua Regia Treatment*

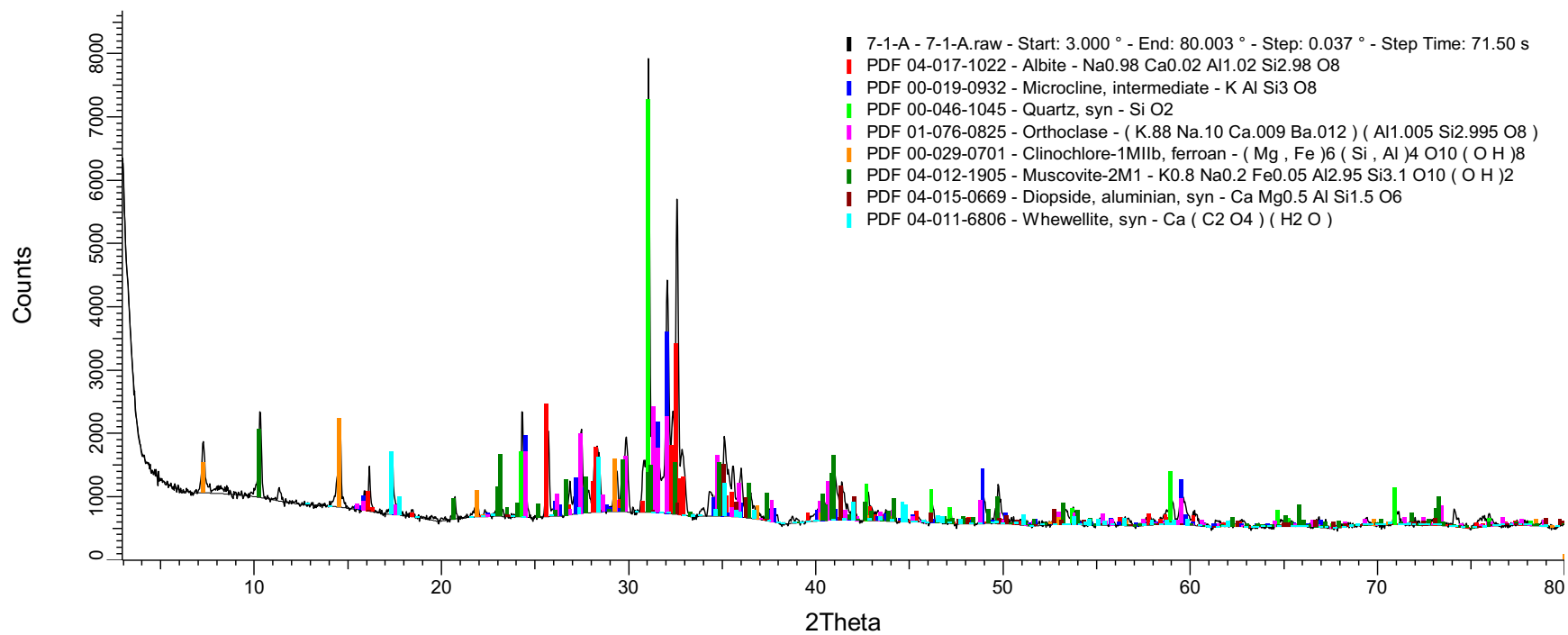


C.2 Site 7 (Hazeltine Creek midway between the TSF and Quesnel Lake)

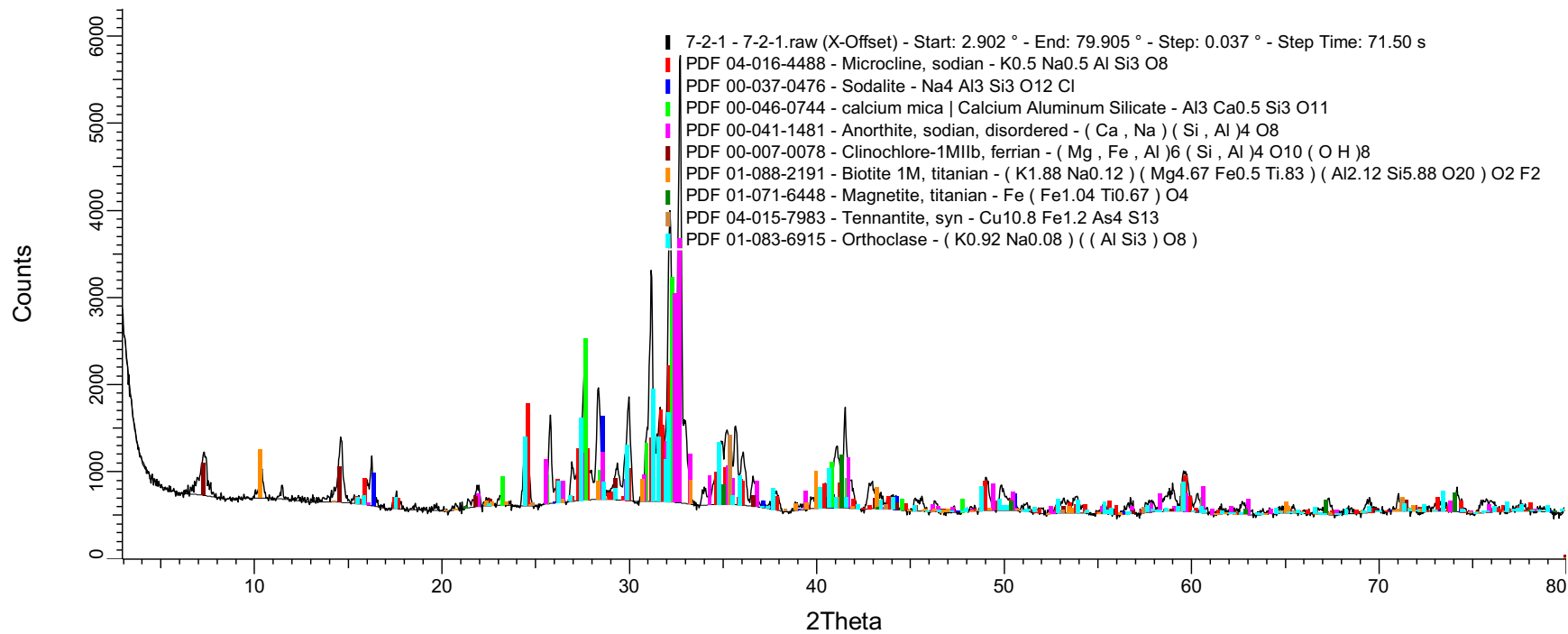
- No Treatment



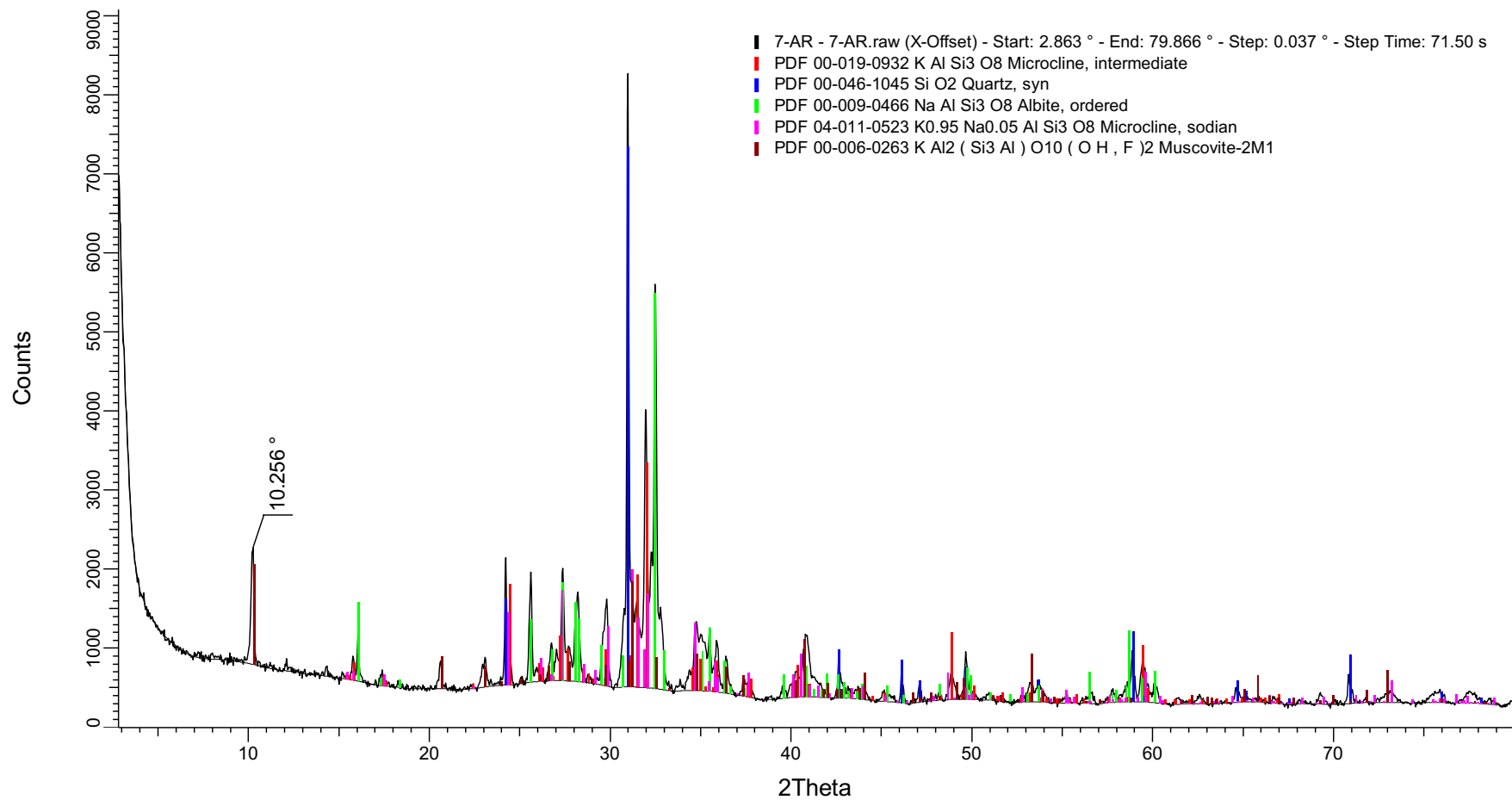
- Acid Ammonium Oxalate Treatment



- Hydrochloric Acid Treatment

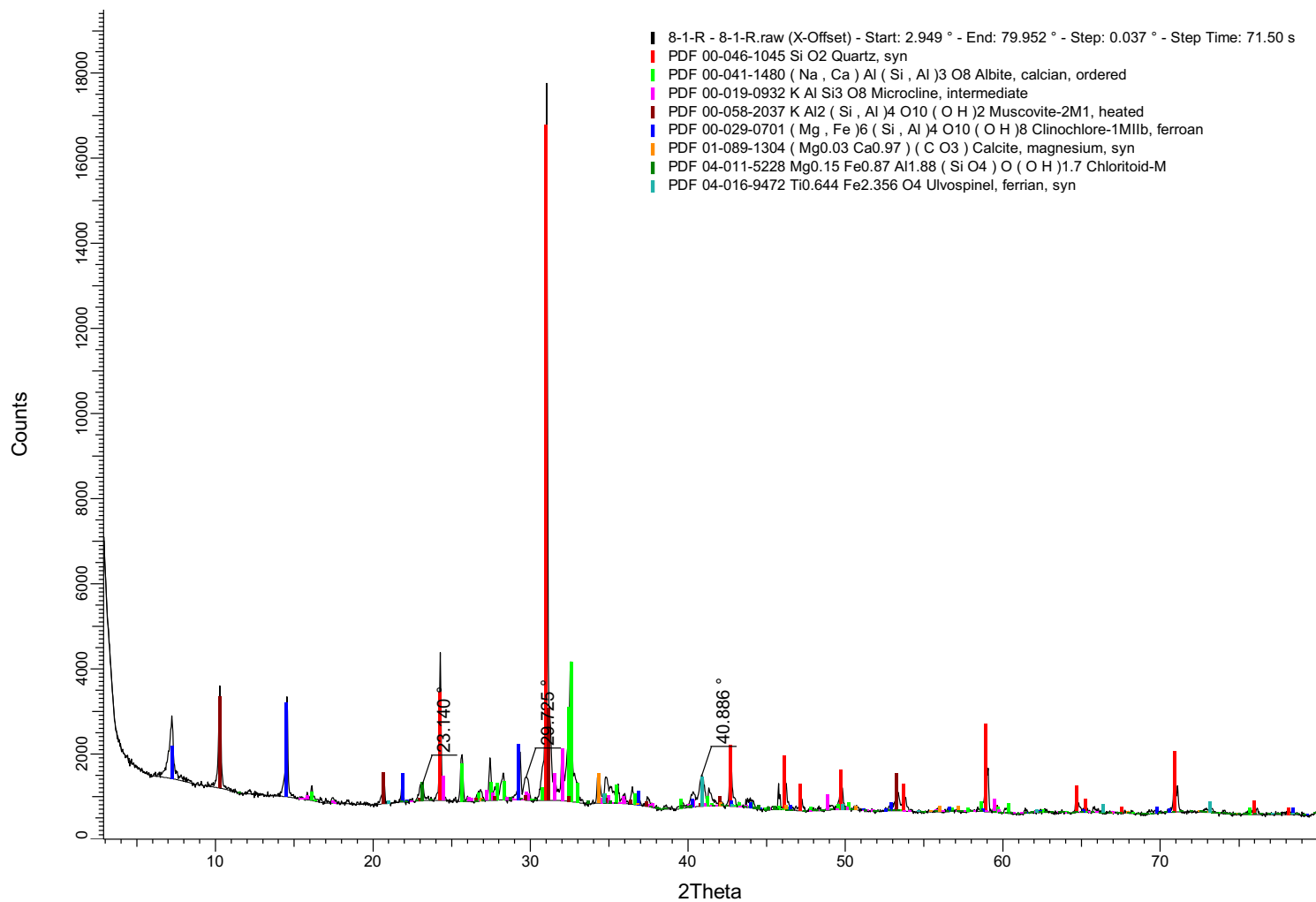


- *Aqua Regia Treatment*

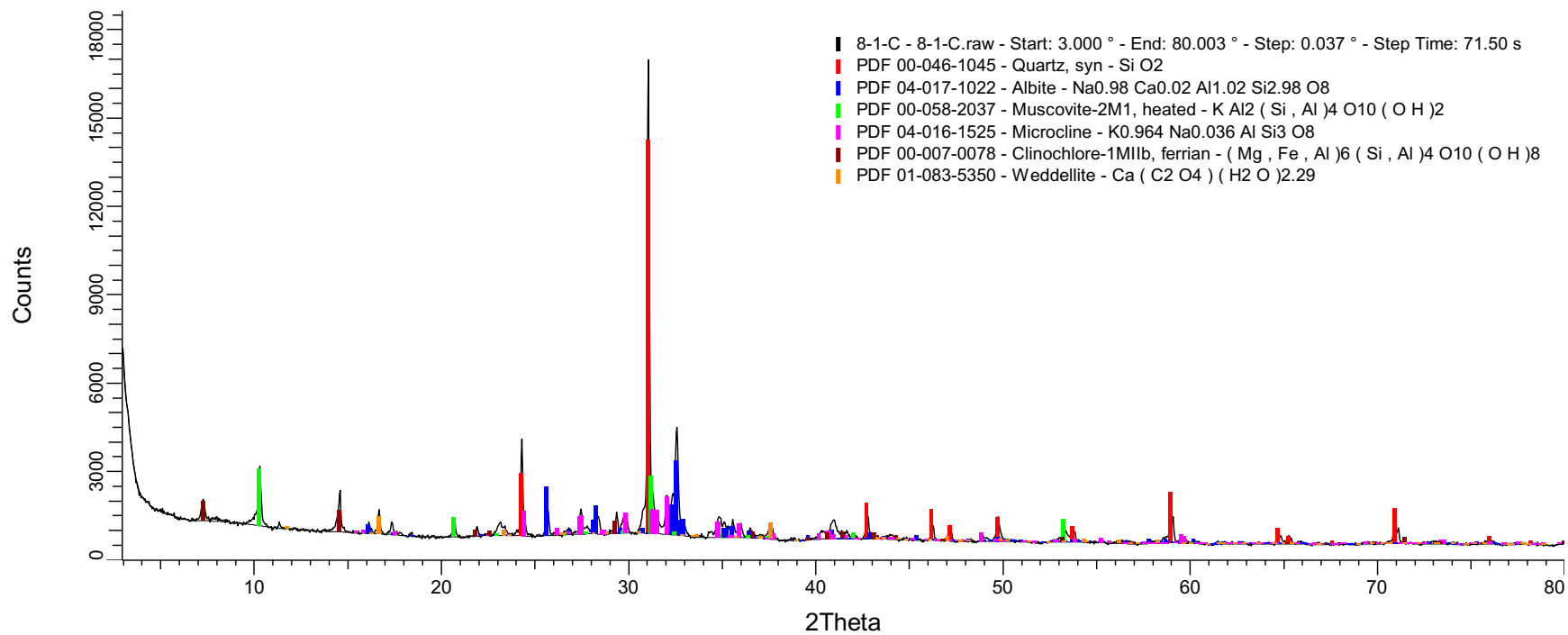


C.3 Site 8 (Lower Hazeltine Creek – Tailings mixed with till)

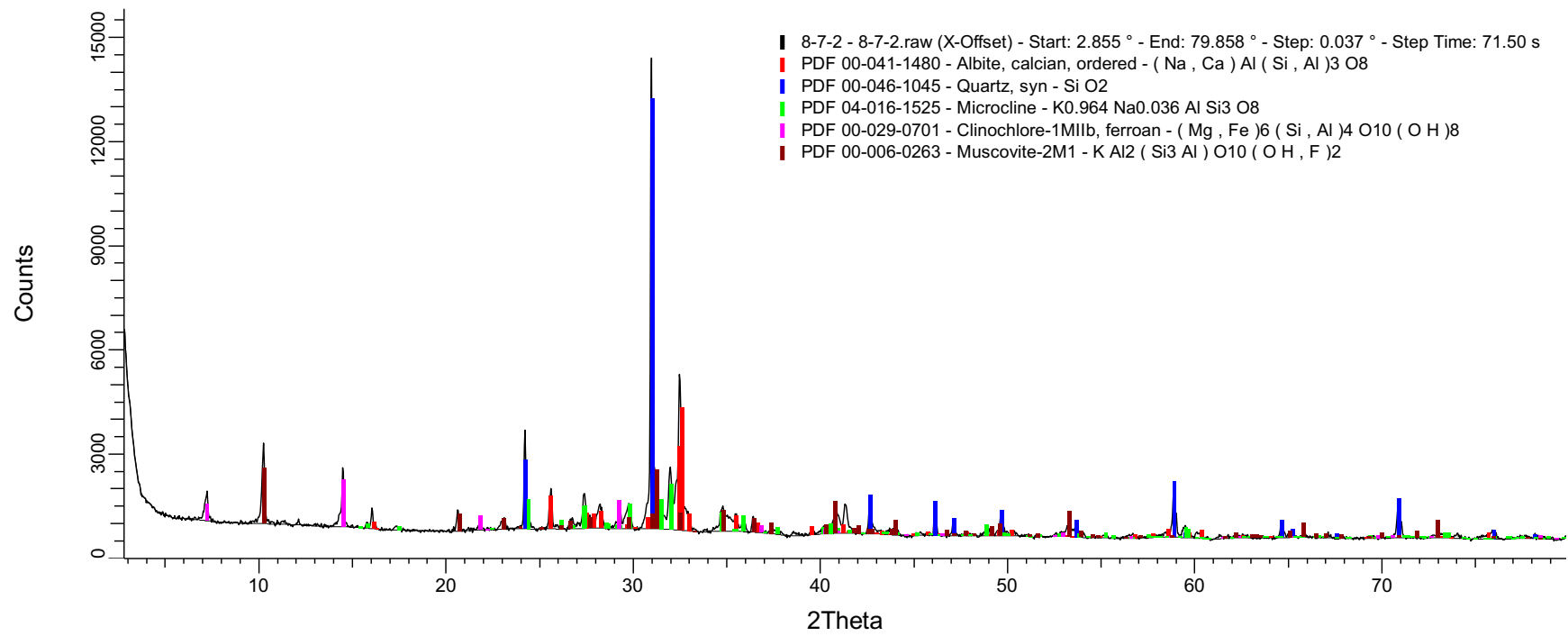
- No Treatment



- Acid Ammonium Oxalate Treatment



- Hydrochloric Acid Treatment



• *Aqua Regia* Treatment

