The Geochemistry, Distribution and Mobility of Metals About an Abandoned Cu-Pb-Zn Mine at Mount Bulga, Orange, NSW: Implications for Acid Rock Drainage

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Abstract
Mining activities at the abandoned Mount Bulga Cu-Pb-Zn-Ag deposit resulted in large amounts of previously buried sulfides being brought to the surface causing the potential of acid mine drainage to be a problem or concern. The pH values measured in the surface soils range from strongly acidic to neutral (3.6-7.9) but averaging mildly acidic (5.2). The distribution of metals in the soils show a distinct zonation between the different geological units clearly defining fault contacts between these units. The XRF analysis using the portable XRF was compared to a laboratory XRF instrument and most metals correlated well except for vanadium, barium and thorium. The highest concentrations of metals were detected about the old mine sites and slag heap as well as related to exposed regions of the shear zone. The mobility of the metals Cu, Pb, Ni and Cr were determined with the order of mobility based on the percentage of total metal concentration mobile as Cu>Pb≈Ni>Cr. Zn was below the limit of detection for the dilutions used. Metal mobility and mineral associations were discovered for Pb and Cu with these metals more mobile with the increase in quartz and less mobile with the increase in actinolite, hornblende, vermiculite and cordierite. Total Cr and Ni concentrations had associations with minerals also with the increase in Ni and Cr concentrations with the increase of hornblende, vermiculite, cordierite, actinolite and a decrease with quartz. Profile analysis demonstrated chromium and nickel associated with parent material or immobile phases at depth, while copper may be a result of dispersion although remaining mostly in the surface soil. Soil particle size analysis determined the surface soils at Mount Bulga to be mainly silt loam with some minor occurrences of sandy loam and silt. The highest average sand content was in the soils overlying the Mullions Range, while the highest average clay content was related to soils of the Anson Formation. Profile samples were predominantly silt loams and profile MBP2 demonstrated a decrease in sand and increase in silt and clay with depth, although one point had the opposite trend. Mineralogy investigations of soils overlying the different geological units determined different mineral associations between the soils. The soil overlying the Byng Volcanics contained tremolite, hornblende, cordierite, actinolite and quartz as the major mineral phases. The soil overlying the Mullions Range Volcanics contained quartz as the major mineral phase with common trace amounts of mixed-layer illite-smectite and chlorite. The soil overlying the Anson Formation contained quartz, chlorite and muscovite as the major mineral phases with common trace amounts of mixed-layer illite-smectite, kaolinite, gypsum and biotite. Profile MBP2 determined a change of mineralogy with depth in both the sand and silt/clay fractions with quartz suddenly dropping to trace amounts at 115 cm depth while vermiculite, cordierite, actinolite, tremolite and hornblende increased from this depth down. Mineralogy investigations identifying proportions of clay minerals in the soils along with total organic carbon content estimated the cation exchange capacity of the soils to be fairly low, though this increased with depth. There is ongoing remediation of the mine site and limestone drains have been placed along the path of drainage. These show virtually no signs of iron precipitation and water in the creeks also show no sign of iron precipitation. A localised map surrounding the mine site appears to show a slight downhill migration from the mine site.

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The Geochemistry, Distribution and Mobility of Metals About an Abandoned Cu-Pb-Zn Mine at Mount Bulga, Orange, NSW: Implications for Acid Rock Drainage

by

Daniel Knight

A thesis submitted in part fulfilment of the requirements of the Honours degree of Bachelor of Science in the School of Earth and Environmental Sciences, University of Wollongong 2014.
The information in this thesis is entirely the result of investigations conducted by the author, unless otherwise acknowledged, and has not been submitted in part, or otherwise, for any other degree or qualification.

Daniel Knight
15/10/2014
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Abstract

Mining activities at the abandoned Mount Bulga Cu-Pb-Zn-Ag deposit resulted in large amounts of previously buried sulfides being brought to the surface causing the potential of acid mine drainage to be a problem or concern. The pH values measured in the surface soils range from strongly acidic to neutral (3.6-7.9) but averaging mildly acidic (5.2). The distribution of metals in the soils show a distinct zonation between the different geological units clearly defining fault contacts between these units. The XRF analysis using the portable XRF was compared to a laboratory XRF instrument and most metals correlated well except for vanadium, barium and thorium. The highest concentrations of metals were detected about the old mine sites and slag heap as well as related to exposed regions of the shear zone. The mobility of the metals Cu, Pb, Ni and Cr were determined with the order of mobility based on the percentage of total metal concentration mobile as Cu>Pb≈Ni>Cr. Zn was below the limit of detection for the dilutions used. Metal mobility and mineral associations were discovered for Pb and Cu with these metals more mobile with the increase in quartz and less mobile with the increase in actinolite, hornblende, vermiculite and cordierite. Total Cr and Ni concentrations had associations with minerals also with the increase in Ni and Cr concentrations with the increase of hornblende, vermiculite, cordierite, actinolite and a decrease with quartz. Profile analysis demonstrated chromium and nickel associated with parent material or immobile phases at depth, while copper may be a result of dispersion although remaining mostly in the surface soil. Soil particle size analysis determined the surface soils at Mount Bulga to be mainly silt loam with some minor occurrences of sandy loam and silt. The highest average sand content was in the soils overlying the Mullions Range, while the highest average clay content was related to soils of the Anson Formation. Profile samples were predominantly silt loams and profile MBP2 demonstrated a decrease in sand and increase in silt and clay with depth, although one point had the opposite trend. Mineralogy investigations of soils overlying the different geological units determined different mineral associations between the soils. The soil overlying the Byng Volcanics contained tremolite, hornblende, cordierite, actinolite and quartz as the major mineral phases. The soil overlying the Mullions Range Volcanics contained quartz as the major mineral phase with common trace amounts of mixed-layer illite-smectite and chlorite. The soil overlying the Anson Formation contained quartz, chlorite and muscovite as the major mineral phases with common trace amounts of mixed-layer illite-smectite, kaolinite, gypsum and biotite. Profile MBP2 determined a change of mineralogy with depth in both the sand and silt/clay fractions with quartz suddenly dropping to trace amounts at 115 cm depth while vermiculite, cordierite, actinolite, tremolite and hornblende increased from this depth down. Mineralogy investigations identifying proportions of clay minerals in the soils along with total organic carbon content estimated the cation exchange capacity of the soils to be fairly low, though this increased with depth. There is ongoing remediation of the mine site and limestone drains have been placed along the path of drainage. These show virtually no signs of iron precipitation and water in the creeks also show no sign of iron precipitation. A localised map surrounding the mine site appears to show a slight downhill migration from the mine site.
Chapter 1: Introduction
Mining activities have and continue to play an important role in producing the raw materials required to maintain and advance the current state of technology and society (Giurco and Cooper 2012). The act of mining though usually results in the removal of geologic material from a buried state not in significant contact with the surface environment. When brought to the surface, mined material containing minerals that would otherwise be stable at depth, are now in a totally different reactive environment which may result in the breakdown of these minerals releasing elements into the environment in such concentrations that they become detrimental to the current population of plants and animals, including people (Ashley et al. 2004). Many trace metals of interest, such as copper, lead and zinc, are enriched in deposits as sulfide minerals commonly alongside large amounts of pyrite, an iron sulfide (Seal Ii et al. 2008). It is the weathering of these sulfide minerals, particularly pyrite, which can cause serious environmental problems with the creation of acidic solutions when they oxidise resulting in the release of metals at problematic concentrations (Druschel et al. 2004, Johnson and Hallberg 2005). There have been numerous studies in Australia and around the world describing and discussing the problems of acid mine drainage (Lottermoser et al. 1999, Ashley et al. 2004, Druschel et al. 2004, Sánchez España et al. 2005). Throughout eastern Australia there are numerous occurrences of small abandoned mine sites that operated under different rules and regulations during the late nineteenth and early twentieth century, with no precaution or care against possible acid mine drainage and the destruction of the local environments (Lottermoser et al. 1999). One of these abandoned mine sites that was operational in the late 1800’s and early 1900’s was the Mount Bulga Copper Mine. This mine site lies within the Lachlan Fold Belt on the western edge of the Hill End Trough, just east of Orange in NSW and was targeting a Cu-Pb-Zn-Ag volcanic hosted massive sulfide deposit that had been remobilised into a shear zone.

The purpose of this investigation was to measure physical and chemical characteristics of soils about the Mount Bulga Copper Mine and shear zone to determine if there is any significant acid mine drainage problems associated with the abandoned mine workings, including the slag heap. This thesis attempts to determine the effect mineralogy may have on total metal distribution both across the land surface as well as with depth. The potential mobility of metals was also studied to attempt to determine the concentrations of metals that may potentially be problematic and whether this may be attributable to the present distribution of metals. Soil profiles were investigated to determine metal mobility with depth and potentially discover the beginning of the effects of mining in the locality. There
has been a previous study on the distribution of metals at Mount Bulga but this focused on the northern part of the shear zone (Xie and Dunlop 1988).
Chapter 2: Literature Review

2.1 Regional Geology
The abandoned mine site of Mount Bulga Copper Mine is situated within the north eastern area of the exposed Lachlan Fold Belt on the western edge of what is known as the Hill End Trough in NSW. The Lachlan Fold Belt itself is part of a larger geological feature known as the Tasmanides which consists of a series of three orogenic zones; 1) Delarmerian, 2) Lachlan Fold Belt and 3) New England Orogen. These formed progressively eastward along the eastern edge of the Australian continent between the Neoproterozoic and the Mesozoic (Foster and Gray 2000). These orogens formed by the accretion of elements such as island arcs, as well as previously rifted continental fragments and subduction related thrust wedges consisting of oceanic crust and continental detritus mostly consisting of turbidite deposits (Foster and Gray 2000).

2.1.1 Lachlan Fold Belt
The Lachlan Fold Belt is not the same across its approximately 700 km width with differences in rock types, metamorphic grade and geological history defining three recognisable zones, split according to the north-south trend of the fold belt, into the western, central, and eastern Lachlan Fold Belt (Foster and Gray 2000). The eastern Lachlan Fold Belt, which Mount Bulga is situated within, is believed to have formed by the accretion of an ocean island arc system of Ordovician age that was situated off the eastern coast of the Australian continental margin (Glen et al. 1998). The accretion of this subduction related volcanic arc system has resulted in three major volcanic belts, namely the Junee-Narrromine Volcanic Belt, the Molong Volcanic Belt and the Rockley-Gulgong Volcanic Belt, which it is believed were all part of the one arc, known as the Macquarie Arc, that became broken during the act of accretion and then later separated due to rifting phases during the Silurian and Devonian (Percival and Glen 2007). One of these extensional rifting phases during the late Silurian to early Devonian resulted in the opening of the Hill End Trough (Collins 2002).

2.1.2 Hill End Trough
The Hill End Trough (Figure 2.1), which is roughly 260 km long in the north-south direction and 70 km at its widest, is bound to the west by the Copperhannia Thrust and Molong Volcanic Belt and in the east by the Wiagdon Thrust and Rockley-Gulgong Volcanic Belt while to the north it is lost underneath the Sydney-Bowen and Great Artesian Basins (Gilligan and Scheibner 1978). The Hill End Trough is thought to have been a marginal sea as no oceanic crust has been found within this structure and so it formed a deep water environment by the thinning and subsidence of the continental crust during extension.
During this extensional phase and its lifetime as a marginal sea the Hill End Trough was extensively affected by felsic and intermediate to mafic magmatism while sedimentation within the trough consisted mainly of deep water turbidites with shallow water shelf sedimentation on the margins (Pogson and Watkins 1998). It is believed that this deep water marginal sea environment lasted until the Middle Devonian when widespread shortening of the Hill End Trough occurred via folding and thrusting that was accompanied by uplift (Glen and Watkins 1999). Further widespread deformation by folding and thrusting occurred in the Hill End Trough during the Early Carboniferous due to the Kanimblan Orogeny which is believed to be the terminal tectonic event that affected the Hill End Trough and the Lachlan Fold Belt (Powell et al. 1976). Erosion and weathering since this event has produced the current geology.

Figure 2.1 Regional map of Hill End Trough showing Mount Bulga just east of Orange. After Gilligan and Scheibner (1978).
2.2 Local Geology

In the vicinity of the abandoned Mount Bulga Copper Mine the outcropping local geology is characterised by formations from the Cabonne and Mumbil Groups. The Cabonne Group represents volcanic phases from the late Middle Ordovician to the Early Silurian that erupted along the Molong Volcanic Belt depositing volcanic rocks of intermediate to mafic composition and of medium potassium to shoshonitic affinity (Pogson and Watkins 1998). Also representative of the Cabonne Group are the associated volcaniclastic detritus and turbiditic sequences that formed alongside these volcanic events including shallow water carbonate reef sequences (Pogson and Watkins 1998). During the Early Silurian the Cabonne Group experienced deformation as well as uplift and erosion (Pogson and Watkins 1998). The majority of the late Early Silurian to earliest Devonian Mumbil Group unconformably overlies the Cabonne Group and represents the beginning of shelf sedimentation in the Hill End Trough and a change in the volcanic character of the region to more felsic volcanism of rhyolitic to dacitic composition (Pogson and Watkins 1998). The group is characterised by thick carbonate and shale sequences associated with felsic volcanic rocks on the shelf margin which were later covered by thin bedded turbiditic siltstone (Pogson and Watkins 1998). The formations associated with these two groups that outcrop at the abandoned Mount Bulga Copper Mine are the Byng Volcanics of the Cabonne Group and the Mullions Range Volcanics and Anson Formation of the Mumbil Group (Figure 2.2).

Figure 2.2 Local geology map. Sampled from Corby (1997).
Figure 2.3 Local geology of Mount Bulga and transects. Faults and geology derived from Geology 250k NSW Statewide 2003, Copyright © NSW Department of Primary Industries 2003. The geology may be slightly out for the local scale.
2.2.1 Byng Volcanics
The Byng Volcanics, according to Pogson and Watkins (1998), extend in a south to southeast direction from the abandoned Mount Bulga Mine east of Orange towards Guyong and Newbridge while faulted blocks occur farther east and southeast of the abandoned Mount Bulga Mine. However Crawford et al. (2007) found that the Byng Volcanics appear to be petrographically different northeast and east of Blayney and so the main belt of Byng Volcanics may only extend as far as Guyong. The Byng Volcanics are characterised by flows of basaltic to andesitic composition along with associated volcaniclastic sequences (Pogson and Watkins 1998). The mineralogy of the Byng Volcanics are reported to include phenocrysts of olivine, plagioclase and augite while greenschist metamorphic alteration has produced overprinting of the basalts with mainly actinolite, albite, calcite, chlorite, epidote, quartz, pumpellyite and tremolite (Pogson and Watkins 1998). In the vicinity of the abandoned Mount Bulga Mine the Byng Volcanics are unconformably overlain by and are in fault contact with the Anson Formation.

2.2.2 Anson Formation
The Anson Formation, according to Pogson and Watkins (1998), is found within the core of the Mullions Range anticline and within several fault slices ranging from the area of Clifton Grove in a south-easterly direction to the area of Kings Plains. It lies unconformably over sections of the Byng Volcanics, is overlain conformably by the Mullions Range Volcanics, and for much of its strike length is in fault contact with Ordovician to Devonian age rocks (Pogson and Watkins 1998). The Anson Formation is well folded and consists of a conglomerate layer at its base overlain by calcareous sediments and limestones which in turn are overlain by mainly pyritic siltstone interlayered with felsic volcanic and volcaniclastic rocks, and some more minor limestone (Pogson and Watkins 1998). Minerals within the formation includes white quartz and remnants of augite and plagioclase within the basal conglomerate layer with the augite and plagioclase probably associated with the Byng Volcanics, while crystals of quartz, biotite, feldspar, and cordierite are associated with the rhyolitic lavas and pyroclastic rocks interlayered with the siltstone of the upper portion of the formation (Pogson and Watkins 1998). Metamorphism has been responsible for the formation within the conglomerate layer of minerals such as tremolite, actinolite, quartz, albite, chlorite, green biotite, epidote and pumpellyite, while within the rhyolitic volcanic rocks metamorphism has created manganese-rich epidote, chlorite, sericite, and sphene minerals (Pogson and Watkins 1998). It is within this formation that the volcanic hosted massive sulfide deposit associated with the abandoned Mount Bulga Copper Mine was formed, being interbedded with limestone, rhyolitic volcanic rocks, and siltstone of the
upper portion of the Anson Formation (Pogson and Watkins 1998). Mineralisation of this
deposit includes pyrite, pyrrhotite, chalcopyrite, sphalerite, galena, with minor cubanite,
marcasite, arsenopyrite, tetrahedrite, native silver, and gold (Pogson and Watkins 1998).
This deposit lies adjacent to the overlying felsic Mullions Range Volcanics.

2.2.3 Mullions Range Volcanics
The Mullions Range Volcanics according to Pogson and Watkins (1998) extend from north
and east of Orange with further faulted sections to the southeast and northwest of Orange.
The lavas that constitute the Mullions Range Volcanics are rhyolitic to dacitic and contain
phenocrysts of quartz and albitised plagioclase with a groundmass made up of very fine
quartz, plagioclase, and sericite (Hilyard 1981). The Mullions Range Volcanics to the east
of Orange where the abandoned mine site sits are characterised by rhyolitic lavas,
ignimbrites, airfall tuffs, pyritic siltstone and black shales that have been regionally
metamorphosed to give manganese-rich epidote, clinozoisite, biotite, chlorite, quartz,
sphene, carbonates and sericite (Pogson and Watkins 1998). Due to the characteristics of
the volcaniclastic rocks and presence of the black shale beds it is believed the Mullions
Range Volcanics were deposited in a deep marine environment at least below storm weather
wave-base and that the limestone that is present was probably emplaced by mass flows
(Hilyard 1981, Pogson and Watkins 1998). The deep water environment that this volcanic
system is thought to have formed in would be ideal for the formation of a volcanic hosted
massive sulfide deposit.

2.3 Volcanic Hosted Massive Sulfide Deposits
At the abandoned Mount Bulga Copper Mine the mineralisation that was of interest is
related to a stratabound volcanic hosted massive sulfide deposit that has been broken up and
volcanic hosted massive sulfide deposits form in deep water environments during
extensional phases where the deposits seem to require submarine depressions such as
calderas which can trap the sulfides that precipitate out of hydrothermal fluids related to the
volcanism. These depressions allow sulfide mineralisation to be preserved by protecting it
from being washed away, dissolved or oxidised, and as they are topographic lows they are
more likely to be covered over by sediments (Ohmoto 1996). The vast majority of all
volcanic hosted massive sulfide deposits form broad mound-like structures, much broader
than their height, which host the majority of the possible Cu-Zn-Pb sulfide mineralisation
while beneath this mound in altered footwall rocks, usually felsic volcanic rocks, is a
stockwork pipe of disseminated pyrite to pyrrhotite which is probably the feeder system for
the hydrothermal fluids (Large 1992, Ohmoto 1996). There have been three different ore types recognised at Mount Bulga that are related to the volcanic hosted massive sulfide deposit, those being the main lenticular polymetallic sulfide ore body, a stockwork of siliceous sulfides and quartz surrounded by altered volcanic rocks and sediments, and finally sulfides that have been remobilised into a shear zone west of the main ore body (Pogson and Watkins 1998). Weathering of the sulfides from this shear zone has resulted in the formation of gossanous outcrops that were the focus of early mining activities.

2.4 Supergene enrichment
Sulfide minerals at the surface or close to the surface that are exposed to the atmosphere tend to become oxidised or break down releasing metals into groundwater which, over time can result in the depletion or dispersion of metals about this weathered zone and as the water carries them downwards cause enrichment farther down the profile (Robb 2005). This process is known as supergene enrichment and an idealised profile of this, based on Cu-Pb-Zn sulfide mineralisation (Figure 2.4), is the formation of a hematite-goethite capping at the surface depleted in most of the original metals followed by zones where these metals have formed secondary minerals of firstly phosphates, then carbonates, and then sulfates, after which there is a zone usually at the water table where secondary sulfide minerals may form before finally reaching the unweathered sulfide minerals that are preserved in a reducing environment (Scott et al. 2001).

Figure 2.4. Idealised Cu-Zn-Pb gossan weathering profile (Scott et al. 2001).
Oxidation of these minerals is commonly attributed to the formation of sulfuric acid from the breakdown of pyrite as shown in (Eqn 1) and further acid production can occur when
the aqueous ferrous iron generated by pyrite breakdown reacts with water and oxygen to form goethite as shown in (Eqn 2) (Robb 2005).

\[
2\text{FeS}_2(s) + 7\text{O}_2(aq) + 2\text{H}_2\text{O}(l) \rightleftharpoons 2\text{Fe}^{2+}(aq) + 4\text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) \quad (\text{Eqn 1})
\]

\[
2\text{Fe}^{2+}(aq) + 3\text{H}_2\text{O}(l) + \text{O}_2(aq) \rightleftharpoons 2\text{FeOOH}(s) + 4\text{H}^+(aq) \quad (\text{Eqn 2})
\]

The resulting acidic solutions help to encourage the breakdown of other sulfide minerals such as chalcopyrite as shown in (Eqn 3) (Robb 2005).

\[
4\text{CuFeS}_2(s) + 17\text{O}_2(aq) + 10\text{H}_2\text{O}(l) \rightleftharpoons 4\text{Fe(OH)}_3(s) + 4\text{Cu}^{2+}(aq) + 8\text{SO}_4^{2-}(aq) + 8\text{H}^+(aq) \quad (\text{Eqn 3})
\]

Volcanic hosted massive sulfide deposits in the Eastern Lachlan Fold Belt typically show weathering to about 20 metres depth though this may extend farther to depths of approximately 60 metres along structures such as faults (Scott et al. 2001). Investigations carried out on the gossans located at Mount Bulga have not found any significant secondary minerals within the gossans except for minor pyromorphite and cassiterite and the weathered gossans appears to extend down to at least 20 metres below the surface with dispersion taking place along faults rather than into the surrounding lithology (Xie and Dunlop 1988). It was these gossans located along a fault zone at Mount Bulga that were targeted for mining activities from the late nineteenth and into the early twentieth century.

### 2.5 Mining History

Mining operations at Mount Bulga first began with the mining of silver after it was discovered there in 1886, but after initial excitement over the possibility of the deposit rivalling Broken Hill, mining for silver at Mount Bulga had ceased by 1889 (Kennedy and Weber 1965). The Mount Bulga Copper mine is believed to have been in operation by 1893 and the workings had been taken over by the Mount Bulga Copper Mining Company by 1901 who were responsible for erecting machinery and sinking a shaft and a drive at about 61 metres below ground (Kennedy and Weber 1965). Following years saw the installation of a blast furnace and the extension of the underground workings with the main shaft reaching a maximum depth of about 91 metres and drives from the main shaft extending south at various levels (Kennedy and Weber 1965). Mining operations at the Mount Bulga Copper Mine probably ceased by about 1912 as records reporting mining activity cease by this time (Kennedy and Weber 1965). Although no photos of the area could be found for the time of mining, an old aerial photo from December 1963 was found and can be compared to the current state of the site as seen in Figure 2.5. These mining activities, that would have exposed sulfide minerals to the atmosphere as well as create spoil and slag heaps, would
have had the potential to cause metal contamination in the surrounding area as these minerals breakdown and disperse.

Figure 2.5 Part of a historic aerial photo showing Mount Bulga Copper Mine (Air Photo Library 1963) compared to 2014 (ESRI Online Basemap World Imagery)

2.6 Acid Mine Drainage
Acid mine drainage is a problem caused by mining activities as they expose large amounts of sulfide materials to the atmosphere and the hydrologic cycle. Excessive acidity in water exiting a mine site can be caused when workings that would usually be below the water table are reflooded at the end of a mine's life as acidic salts formed by the oxidation of sulfides are dissolved into the water (Johnson and Hallberg 2005). The resulting ore dumps, slag heaps and tailings related to the mine are of even more problematic with the large surface areas now exposed to the passage of both air and water, the reactions creating acidity increase significantly (Johnson and Hallberg 2005). As mentioned before with the formation of goethite, acidity can be increased by the precipitation of iron. This is also important as even though the pH of some waters passing through a mine site may be measured as near neutral, reduced iron and manganese species may still be mobile which can then precipitate later resulting in an increase in acidity (Johnson and Hallberg 2005).
2.7 Metal Mobility

The mobility and dispersion of metals within the environment, either from natural reservoirs or as a result of human activities such as mining and smelting, is an important issue as the potential for adverse effects caused by these metals may result in the ill health or destruction of plants and animals including humans. This has resulted in many countries setting up guidelines and regulations specifying safe concentration limits of metals and other chemicals in the environment where, if these limits are exceeded, action needs to be taken in controlling or removing the hazard. In Australia the guidelines that currently deal with assessment of potentially contaminated sites are outlined within the amended National Environment Protection (Assessment of Site Contamination) Measure 1999 (ASC NEPM 2013). Investigation concentrations for a range of metals is provided in Table 2.1, although this does not cover a site like Mount Bulga, the section C is the most similar covering outdoor open space. Apart from the potentially damaging effects of mobilised metals to the surrounding environment, they may also be of significance in exploration for potential resources or measuring the fertility of agricultural land (VanLoon and Duffy 2010, Lintern et al. 2013). The mobility of metals within the soil environment is complicated as it is affected by numerous physical, chemical and biological properties of the soil, such as pH, oxidation and reduction potential, mineralogy, organic matter content, adsorption and desorption reactions, plant and microbial activity, and reactions involving precipitation or dissolution (McLean and Bledsoe 1992, Chaignon et al. 2003, Simon et al. 2010).

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Health-based investigation levels (mg/kg)</th>
<th>Residential A</th>
<th>Residential B</th>
<th>Recreational C</th>
<th>Commercial/industrial D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals and Inorganics</td>
<td></td>
<td>Residential A</td>
<td>Residential B</td>
<td>Recreational C</td>
<td>Commercial/industrial D</td>
</tr>
<tr>
<td>arsenic</td>
<td></td>
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<td>3000</td>
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<td>beryllium</td>
<td></td>
<td>70</td>
<td>100</td>
<td>100</td>
<td>500</td>
</tr>
<tr>
<td>boron</td>
<td></td>
<td>5000</td>
<td>40000</td>
<td>20000</td>
<td>300000</td>
</tr>
<tr>
<td>cadmium</td>
<td></td>
<td>20</td>
<td>140</td>
<td>100</td>
<td>800</td>
</tr>
<tr>
<td>chromium (VI)</td>
<td></td>
<td>100</td>
<td>500</td>
<td>240</td>
<td>3000</td>
</tr>
<tr>
<td>cobalt</td>
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<td>600</td>
<td>300</td>
<td>4000</td>
</tr>
<tr>
<td>copper</td>
<td></td>
<td>7000</td>
<td>30000</td>
<td>20000</td>
<td>250000</td>
</tr>
<tr>
<td>lead D</td>
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<td>300</td>
<td>1200</td>
<td>600</td>
<td>1500</td>
</tr>
<tr>
<td>manganese</td>
<td></td>
<td>3000</td>
<td>8000</td>
<td>9000</td>
<td>40000</td>
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<tr>
<td>methyl mercury</td>
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<td>7</td>
<td>30</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td>mercury (inorganic)</td>
<td></td>
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<td>600</td>
<td>400</td>
<td>4000</td>
</tr>
<tr>
<td>nickel</td>
<td></td>
<td>400</td>
<td>900</td>
<td>800</td>
<td>4000</td>
</tr>
<tr>
<td>selenium</td>
<td></td>
<td>200</td>
<td>1500</td>
<td>700</td>
<td>10000</td>
</tr>
<tr>
<td>zinc</td>
<td></td>
<td>8000</td>
<td>60000</td>
<td>30000</td>
<td>400000</td>
</tr>
</tbody>
</table>

Table 2.1 Investigation concentrations for metals and metalloids (ASC NEPM 2013).

The pH of a soil is one of the most important properties of a soil in regards to metal mobility as it has been shown that as pH decreases many metal cations become increasingly mobile (McLean and Bledsoe 1992) while oxyanionic species of metalloids such as arsenic can
become more mobile as pH increases (McLean and Bledsoe 1992, Simon et al. 2010, Romero-Freire et al. 2014). The change in mobility of the metals, due to pH, is in part caused by greater adsorption onto solid soil phases by hydrolysed species compared with that of the free metal ion (James et al. 1975, McLean and Bledsoe 1992), but is also due in part to the pH dependence of some soil components adsorption sites, which become less negatively charged as pH decreases, favouring the adsorption of anions and the desorption of cations at these sites (McLean and Bledsoe 1992, VanLoon and Duffy 2010). These pH dependant sites are the negative charges associated with organic matter, oxide minerals and broken edges of clay minerals while permanently charged sites that are not affected by pH are mineral surfaces where there has been a substitution in the mineral lattice with an element of different charge such as replacing a Si\textsuperscript{4+} ion with an Al\textsuperscript{3+} ion within the tetrahedra of a silicate mineral (McLean and Bledsoe 1992, VanLoon and Duffy 2010).

This ability for a soil to bind mobile ions is known as the cation, or anion, exchange capacity though cation exchange is in most cases the more influential (McLean and Bledsoe 1992). The cation exchange capacity (CEC) of a soil is important as a large CEC can provide a buffer to the release of significant concentrations of metals that may be present in the soil by keeping them bound to exchange sites and lowering their mobility (Simon et al. 2010). The CEC of a soil is dependent on, to some extent, the pH as previously mentioned but also on mineralogy and particle size as, for the same volume, finer particles contribute a larger surface area resulting in many more potential exchange sites (Ersahin et al. 2006, VanLoon and Duffy 2010). Therefore knowing the mineralogy and the particle size of the soils at Mount Bulga may give some insight to the potential cation exchange capacity of the soils and the metal mobility. Although some minerals such as clays can have high CEC, organic matter content can contribute much more to the CEC of the soil (Oorts et al. 2003).

Organic matter also plays an important role in the mobility of metals within the soil as the break down products of organic matter contain acidic functional groups that are able to form metal complexes which can result in the metal being either bound to a solid state, or if the organic matter is dissolved, enhance metal mobility (McLean and Bledsoe 1992). The ability for organic matter to bind metals is also dependant on pH as the lower the pH the more likely functional groups will be protonated and unavailable for forming complexes with the result of freeing complexed metals into solution while an increase in pH will result in the functional groups being available and allowing the formation of metal complexes (McLean and Bledsoe 1992).
2.8 Measuring Metal Mobility
One way of estimating how mobile particular metals are is to perform a chemical extraction on the soils of interest and determine the resulting concentration of the supernatant fluid. There are numerous procedures utilising different reagents that attempt to mimic the natural soil water conditions to measure either the total potential metal mobility or to measure a bound fraction from a particular soil component (Leleyter et al. 2012). These procedures can be either categorised as single or sequential extractions where single extractions are usually designed to estimate the exchangeable fraction while sequential extractions tend to provide information on the metal mobility from particular soil phases by using increasingly aggressive extractants in each sequential step (Sahuquillo et al. 2002, Leleyter et al. 2012). The complexing agent ethylenediaminetetraacetic acid (EDTA) has been used extensively to measure the potential mobility and bioavailability of metals associated with non-silicate bound phases such as organic matter, clay particles, oxides, phosphates and carbonates otherwise thought to be the total exchangeable fraction (Sahuquillo et al. 2003, Labanowski et al. 2008). It has been demonstrated that the highest metal extraction by EDTA occurs when the concentration of EDTA reaches at least 0.05 M and the pH of the extraction varies least at pH values between 5.5 and 7.5, and so these experimental parameters may be ideal for a single extraction (Fangueiro et al. 2002).

2.9 Soils
The soils in the Mount Bulga area have been described previously as skeletal podsols along topographic highs while becoming somewhat thicker with an obvious profile on the slopes and in the valleys (Govett et al. 1984). The major soil profiles of the Mount Bulga area, as described by the Soil Landscapes Bathurst 1:250000 sheet (Kovac et al. 1989), are Red Podzolics and Yellow Soloths based on the Burrendong and Mookerawa landscapes. Some of the Byng landscape soils in the vicinity of Mount Bulga are mainly Brown Clays and Weisenboden. These may be the major soils of the area but soils may vary on a local scale and may include types not listed here. The Australian Soil Classification has reclassified these soils as Kurosols for the Podzolics and Soloths and Vertosols for the Brown Clays and Weisenboden. Kurosols are considered to be soils which have a clearly defined textural B horizon which, at least in the upper part of the B2 horizon, is strongly acidic and may show some unusual chemical behaviour in the subsoil such as high specific elemental content (Isbell 2002). Vertosols are considered to be clay soils that swell when wet and crack when dry, they may have slickensides and lenticular peds at depth (Isbell 2002).
Chapter 3: Methods

3.1 Mapping
A basic map was constructed while in the field using an aerial photograph and tracing paper, recording GPS locations when taking note of outcrop locations as seen on the map and confirmed in the field. Further maps were constructed using ArcGIS 10.2 software back at the university based on the GPS data recorded for outcrop locations and specialised maps based on the XRF data for individual elements.

3.2 Sampling

3.2.1 Outcrop samples
Outcrop samples were taken of the various rock units located within or nearby the transect grid in order to establish metal concentrations of the parent rocks from which the soils have been derived.

3.2.2 Soil samples
Soil geochemistry was performed at 25-100 mm depths using the Niton XL3t portable handheld XRF analyser with GPS locations recorded for each sampling site. Soil testing and geochem was performed at 25 m intervals along east-west transects approximately 500-600 m long and 200 m apart. Approximately 200-250 metre long north south transects were conducted over the abandoned mine site and slag heap areas with sampling also taken at about 25 metre intervals with transects 50 metres apart. Further infill east-west transects of approximately 200-250 metres were also taken over the abandoned mine site and slag heap with sampling every 25 metres and transects about 40-50 metres apart. Physical soil samples of approximately 100 g were collected occasionally using an aluminium hand spade, avoiding large roots and rocks as much as possible, and placed into sealable plastic sample bags, usually when there was a significant change in the copper or lead ppm values indicated by the handheld XRF but also for significant soil characteristic changes.

3.2.3 Profile sediment samples
Sediment profiles were taken from several locations along Black Bulga Creek and just below the abandoned mine site (Figure 3.1). Locations of each attempted profile were recorded using GPS and given an identification code. Profiles at locations MBP1 and MBP3 were taken from the face of the stream bank which had been squared off using a spade from the top of the bank to the water surface (Figure 3.2). Metal content readings of the sediment using the handheld XRF were taken at 100 mm intervals from the base of the profile to the top. Sediment samples were taken if there was a significant change in the copper ppm values. All other profiles were taken by digging an approximately 300 mm deep hole with the spade and then using a hand auger to go deeper (Fig 3.3). Metal content readings of the
soil/sediment were taken using the handheld XRF at 50 mm intervals for the dug hole measured from the top down. The hand auger was then used to go deeper, going to irregular depths determined by how far the auger would efficiently bite into the ground. These depths were measured from a bar across the top of the hole to the base of the auger hole, however this was not the depth of the measured reading as it was taken while the soil/sediment was still in the core of the auger and at a height above the tip of the auger, so this value was subtracted from the depth measurement to get the sample depth. Again physical samples were taken and bagged based on whether there was a significant change in the copper ppm values from the XRF result.

Figure 3.1 Map of profile locations.
Figure 3.2 Profile MBP1 showing spade edge down the side of the bank.
3.3 Sample analysis

3.3.1 Mineral identification of rock samples
Rock samples that were collected from the field site were prepared for petrographic examination via thin section. Polished blocks were also created of gossanous material and a rock containing sulfide mineralisation.

3.3.2 Soil and sediment analysis
Prior to any analysis all soil and sediment samples brought back from the field were initially spread out on plastic trays within a laboratory room, removing roots as much as possible, and allowed to air dry over three days. After the samples were air dried they were then dry sieved through a bronze sieve with a 2 mm stainless steel mesh with some samples that dried as hard aggregates needing to be broken up using a porcelain mortar and pestle before being sieved again. The less than 2mm fractions were then placed into paper soil sample bags.

3.3.2.1 pH
All air dried samples had their pH tested in both deionised water and 0.01 M CaCl₂ solution closely following procedures 16.2 and 16.3 given by Hendershot et al. (2008) although the electrical conductivity of the calcium chloride solution was not measured. It was not possible to test the entire batch of samples on the same day due to the limited availability of suitable sized beakers so tests were spread out over several days. Measurements were
carried out using an Orion 3-star pH bench top meter utilising an Orion 8157BNUMB Ross ultra pH/ATC triode calibrated using green pH 7 buffer 1.09477.0500 and red pH 7 buffer 1.09475.0500 by Centipur. For both deionised water and calcium chloride solution ten grams of sample was mixed with 20 ml of solution.

3.3.2.2 Particle size
The particle size fractions of all collected samples were analysed using the Malvern Instruments Mastersizer 2000 with the Hydro 2000MU accessory. Samples were slowly added to a beaker of water that was being cycled through the instrument and back to the beaker until the obscuration of the instrument was within the desired range. While this was done the sonicator was placed on to disperse any fine clay particles and switched off prior to analysing the sample. Once ready the instrument was set to record the analysis, doing this five times and taking the average of each run.

3.2.2.3 Total metals using laboratory XRF
Total metals in the samples were also analysed using the laboratory AMETEK SPECTRO XEPOS ED-XRF instrument. Firstly all collected profile MBP2 samples and one transect sample were separated into their sand and silt/clay fractions. This was done by dry sieving samples through a 63 µm plastic mesh to collect the silt/clay fraction, then wet sieving the sand fraction through the same mesh after it had undergone ultrasonic cleaning. Preparation for XRF analysis involved crushing approximately 10 g of samples down to a fine powder initially using the chrome-steel ring mill and one using the tungsten carbide ring mill before crushing the remaining samples using an agate mortar and pestle. These differences in use of crushing equipment were due to firstly not knowing that tungsten may mask elements of interest and secondly that an agate mortar and pestle was available to use and would be capable of grinding the sample to a suitable powder and so therefore avoid potential contamination by the chrome-steel ring mill. Approximately four to five grams of the resulting powdered samples were then mixed with polyvinyl alcohol to bind the sample together and then compressed to 200 bar into small pellets within an aluminium cup using a hydraulic press. These were then left to set and dry overnight in an oven at 65°C before being analysed.
3.2.2.4 Mineralogy using XRD
The same powdered samples as described in the previous section were also analysed using the Spellman DF3 X-ray generator utilising a 1kW copper X-ray tube and scanned between 4-70° using a Philips goniometer to determine the mineralogy of the soil/sediment samples. The resulting analysis was then processed to identify the possible mineralogy using software. TRACE V4 software was used to align the trace, shifting the quartz base peak to its proper value. Siroquant v3 software was then used to fit a waveform to the analysed waveform and determine the potential mineralogy of the sample.

3.2.2.5 Metals mobility ICP-MS
The potential metal mobility was examined by performing an extraction using the chelating agent EDTA. A modification of procedure 13.4 by Soon & Abboud (1993) was used where only 2 g of sample was used in 10 ml of 0.05 M EDTA for the unseparated samples while 1 g of sample in 5 ml of 0.05 M EDTA was used for the separated samples due to some samples lacking enough mass. These were placed in 15 ml acid washed plastic centrifuge tubes and strapped to a rotating wheel and left to mix overnight. They were next placed in a centrifuge for several minutes before being filtered through a 0.45 µm filter into 5 ml acid washed plastic vials. After appropriate dilutions of each sample they were analysed by ICP-MS for the metals copper, lead, zinc, chromium and nickel as well as the metalloid arsenic.

3.2.2.6 Approximate Organic Carbon Content
The same samples as used in the XRD and XRF analysis were also analysed for their approximate organic carbon content. This was based on the mass loss on ignition of approximately 1 g samples. A crucible was preheated to 1050°C for 2 hours and then weighed while still warm, then the powdered sample was placed in the crucible and weighed before being heated to 1050°C for another 2 hours. Once this was done the combined mass of the crucible and sample was weighed again. The difference between this last mass and the mass prior to heating gave the mass lost during ignition.
Chapter 4: Results

4.1 Outcrop Samples

4.1.1 Outcrop Samples XRF
Total metal concentrations in outcrop samples collected at locations shown in Fig.4.1 were analysed using the XRF. Full results for this are displayed in Appendix A3 and Table 4.1 displays the values measured for the metals copper, lead, zinc, chromium, nickel and the metalloid arsenic.

Figure 4.1 Outcrop sample locations. No marker for DKMB01.
Table 4.1 Average metal concentrations of outcrop samples.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Cr</th>
<th>Ni</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>DKMB01 Minesite Gossan</td>
<td>3513.16</td>
<td>&lt;LOD</td>
<td>837.98</td>
<td>3597.58</td>
<td>148.48</td>
<td>192.47</td>
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<tr>
<td>DKMB14 Gossan Shearzone</td>
<td>2724.73</td>
<td>4436.31</td>
<td>3061.70</td>
<td>328.96</td>
<td>248.56</td>
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<tr>
<td>DKMB03 Slag</td>
<td>1006.04</td>
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<td>650.60</td>
<td>93.85</td>
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<tr>
<td>DKMB04 Slag</td>
<td>3907.77</td>
<td>28.32</td>
<td>2280.66</td>
<td>777.54</td>
<td>165.41</td>
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<td>5804.83</td>
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<td>216.08</td>
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<td>67.77</td>
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<td>250.31</td>
</tr>
<tr>
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<td>299.65</td>
<td>250.14</td>
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<tr>
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<td>27.25</td>
<td>39.43</td>
<td>&lt;LOD</td>
<td>18.77</td>
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<td>19.85</td>
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<td>&lt;LOD</td>
<td>13.14</td>
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<tr>
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<tr>
<td>DKMB02 Conglomerate Anson?</td>
<td>76.31</td>
<td>15.19</td>
<td>90.51</td>
<td>668.62</td>
<td>127.75</td>
<td>83.67</td>
</tr>
</tbody>
</table>

4.1.2 Thin Sections and Polished Blocks of Rock Samples
Several thin sections were created from outcrop samples gathered in the field. This was done to identify the various mineralogy associated with the different outcropping units, including the slag, which may contribute to the mineralogy of the surrounding soils. Samples were taken from the Byng Volcanics, Mullions Range Volcanics, gossan and ore material from the shear zone, slag, a nearby intrusion, and what may be part of the basal conglomerate layer of the Anson Formation. Thin sections of other Anson Formation samples were not made due to the very fine-grained nature of the siltstone.

4.1.2.1 Byng Volcanics
The Byng Volcanics thin section shows numerous euhedral crystals, some are twinned, that are pleochroic yellow to colourless in plain polarised light and show second order birefringence colours in crossed polarised light, which would seem to suggest they are epidote. There also is one occurrence of a calcite crystal and some plagioclase as well as quartz. The rest of the thin section is groundmass of unidentified mineralisation.
4.1.2.2 Mullions Range Volcanics

The Mullions Range Volcanics thin sections show euhedral phenocrysts of quartz and plagioclase (Fig 4.2), possibly albite due to an approximately 10 degree extinction angle, and there is also some minor occurrences of muscovite, and biotite. These sit within a very fine groundmass of which some is acicular needles of an unidentified mineral which appears to have a preferred orientation.

Figure 4.2 Phenocrysts of quartz (left) and plagioclase (right) in Mullions Range Volcanics.

4.1.2.3 Gossan and Ore

The main minerals of the ore sample appear to be quartz, pyrrhotite, and chalcopyrite (Fig.4.3) with minor amounts of galena and possibly hematite. Pyrrhotite appears to be highly fractured and weathered with some areas looking like they have been entirely altered to possibly goethite and hematite. The mineral assemblage’s texture would suggest it is a hydrothermal vein system.

Figure 4.3 Sulfide mineralisation in ore from mine site.
The gossan sample simply shows botryoidal growth of goethite that has grown out from what appears to be highly weathered, fractured and iron-stained quartz (Fig.4.4). The goethite growth probably replaced sulfides within the fractures but evidence of any sulfides no longer exists.

Figure 4.4 Botryoidal growth of goethite in gossan sample.

4.1.2.4 Slag
Thin sections of slag samples show euhedral crystals forming spinifex textures, some with a distinct feathery appearance while others are long groups of cross-cutting acicular needles (Fig.4.5). In plane polarised light, needles are bright with high relief, while under crossed polarised light they show second order birefringence colours. Some of the slag shows definite layer like zoning with long acicular needles in contact with a zone of smaller broken needles lying roughly perpendicular to the longer ones. In another sample the layering shows a region of crystals with a feathery spinifex texture which borders a region of uniform and undifferentiated minerals, though both regions show second order birefringence colours under crossed polarised light. This zoning is probably due to either cooling edges or the filling of vughs within the slag.
4.1.2.5 Intrusion
The thin section of an intrusion shows highly altered phenocrysts of clinopyroxene, some showing 45 degree cleavage and simple twinning. The groundmass consists of magnetite, quartz, chlorite and some minor muscovite. There appears to be veining throughout the sample which is made up of mainly quartz with some epidote, occasional plagioclase and possibly hematite.

4.1.2.6 Basal Anson Formation
The thin section of a rock taken from above the slag heap which may possibly be the basal layer of the Anson Formation shows numerous magnetite crystals spread throughout. Many minerals appear highly altered showing what looks like frayed edges. There is a large quantity of what may be actinolite which has a greenish colour in plane polarised light with an acicular to tabular appearance with some twinned and all having frayed ends. The groundmass consists of what is probably quartz and has the occasional vein running through it filled with quartz and minor plagioclase. There is a large clast in the thin section which has more actinolite as well as altered clinopyroxene possibly plagioclase.
4.2 Particle Size Analysis
Particle size analysis was performed on the less than 2mm fractions of all samples collected from Mount Bulga to determine the sand, silt and clay fraction of the soil. Combined with the mineralogy of the soil and organic carbon content this may help to estimate the potential cation exchange capacity of the soils. Results have been separated into transect and profile samples.

4.2.1 Transect Samples
Results of the particle size analysis on the transect samples show that the soils about the abandoned Mount Bulga Copper Mine are mainly a silty loam with some minor sandy loams and silt as shown in Figure 4.6.

Table 4.2 shows the sand, silt and clay averages, standard deviations, medians and ranges based on the entire surface soils samples analysed and then separating these into particular areas of the field such as slag heap, mine site and the remaining soil samples.

Table 4.3 shows the sand, silt and clay averages, standard deviations, medians and ranges based on the results separated by the type of geology the soil is believed to be situated above.

![Figure 4.6 surface soil texture showing sand, silt and clay content. Utilising the USDA soil textural diagram.](image-url)
<table>
<thead>
<tr>
<th>Total</th>
<th>Average</th>
<th>Std deviation</th>
<th>Median</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>25.40</td>
<td>11.32</td>
<td>24.36</td>
<td>3.92-62.06</td>
</tr>
<tr>
<td>Silt</td>
<td>68.84</td>
<td>10.63</td>
<td>70.13</td>
<td>34.10-91.00</td>
</tr>
<tr>
<td>Clay</td>
<td>5.75</td>
<td>1.89</td>
<td>5.58</td>
<td>1.64-11.51</td>
</tr>
<tr>
<td><em>Slag heap</em></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sand</td>
<td>24.49</td>
<td>10.14</td>
<td>23.63</td>
<td>9.16-49.89</td>
</tr>
<tr>
<td>Silt</td>
<td>69.35</td>
<td>9.00</td>
<td>70.97</td>
<td>46.90-85.04</td>
</tr>
<tr>
<td>Clay</td>
<td>6.15</td>
<td>2.01</td>
<td>5.65</td>
<td>3.21-11.51</td>
</tr>
<tr>
<td><em>Mine site</em></td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sand</td>
<td>32.21</td>
<td>15.33</td>
<td>26.46</td>
<td>12.88-62.06</td>
</tr>
<tr>
<td>Silt</td>
<td>61.79</td>
<td>13.92</td>
<td>65.94</td>
<td>34.10-81.35</td>
</tr>
<tr>
<td>Clay</td>
<td>6.00</td>
<td>2.67</td>
<td>5.60</td>
<td>1.64-11.05</td>
</tr>
<tr>
<td><em>Other Samples</em></td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sand</td>
<td>23.11</td>
<td>9.02</td>
<td>24.18</td>
<td>3.92-47.40</td>
</tr>
<tr>
<td>Silt</td>
<td>71.55</td>
<td>8.85</td>
<td>70.67</td>
<td>47.16-91.00</td>
</tr>
<tr>
<td>Clay</td>
<td>5.35</td>
<td>1.26</td>
<td>5.56</td>
<td>2.65-8.49</td>
</tr>
</tbody>
</table>

Table 4.2 soil size fraction results based on surface soil location.

<table>
<thead>
<tr>
<th>Byng</th>
<th>Average</th>
<th>Std deviation</th>
<th>Median</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>19.08</td>
<td>8.76</td>
<td>16.29</td>
<td>8.17-47.4</td>
</tr>
<tr>
<td>Silt</td>
<td>75.66</td>
<td>8.67</td>
<td>79.04</td>
<td>47.16-85.29</td>
</tr>
<tr>
<td>Clay</td>
<td>5.25</td>
<td>1.06</td>
<td>5.44</td>
<td>3.51-6.82</td>
</tr>
<tr>
<td><em>Mullions</em></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sand</td>
<td>31.55</td>
<td>6.36</td>
<td>29.70</td>
<td>21.71-40.17</td>
</tr>
<tr>
<td>Silt</td>
<td>63.52</td>
<td>6.45</td>
<td>65.65</td>
<td>53.31-72.73</td>
</tr>
<tr>
<td>Clay</td>
<td>4.93</td>
<td>1.11</td>
<td>5.31</td>
<td>3.62-6.52</td>
</tr>
<tr>
<td><em>Anson</em></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sand</td>
<td>24.26</td>
<td>7.56</td>
<td>24.44</td>
<td>3.92-33.43</td>
</tr>
<tr>
<td>Silt</td>
<td>70.08</td>
<td>7.19</td>
<td>70.10</td>
<td>62.77-91.00</td>
</tr>
<tr>
<td>Clay</td>
<td>5.66</td>
<td>1.54</td>
<td>5.72</td>
<td>2.65-8.49</td>
</tr>
</tbody>
</table>

Table 4.3 soil size fraction results based on underlying geology.
4.2.2 Profile Samples
The soil texture of the profile samples show they are also predominantly silty loams although they contain much less sand compared to the majority of transect surface soil samples as shown in Figure 4.7.

Figure 4.8 shows the downward trend of the sand, silt and clay fractions in profile MBP2.

![USDA soil textural diagram](image)

Figure 4.7 profile texture showing sand, silt and clay content. Utilising the USDA soil textural diagram.
4.3 Mineralogy

4.3.1 XRD of Soil/Sediment Samples
The subset of surface samples chosen for XRD analysis allowed a comparison of results between soils overlying the different geological units around Mount Bulga. The results of the analysis were based on soils overlying the Byng Volcanics, the Mullions Range Volcanics and the Anson Formation as well as some probable erosional sediments located near drainage channels and Black Bulga Creek. The mineralogy of profile MBP2 was also identified to determine if there is a change in mineralogy with depth. Full results of the XRD analysis are displayed in Appendix B1.

4.3.1.1 Transect Samples
The surface samples of the soils located on the Byng Volcanics show an apparent mineralogical difference to those found near outcrops of Mullions Range Volcanics, Anson Formation, and those made up of probable erosional sediments. The main minerals identified making up the soils related to the Byng Volcanics are quartz, tremolite, actinolite, hornblende and cordierite, with some minor albite and chlorite. Figure 4.9 shows the relative percentages of those minerals identified for the various soil samples believed to overlie the

Figure 4.8 soil size fraction change with depth for profile MBP2.
Byng Volcanics. The soils believed to overlie the Mullions Range Volcanics and Anson Formation show higher relative proportions of quartz than those over the Byng Volcanics and lack some of the minerals associated with the Byng Volcanics. The main mineral in the soils overlying the Mullions Range Volcanics is quartz at 60% or more with minor amounts of chlorite, muscovite, hornblende and mixed-layer illite-smectite. Figure 4.10 shows the relative percentages of those minerals identified for the soils believed to overlie the Mullions Range Volcanics. The soils overlying the Anson Formation are similar to the Mullions range volcanics but with slightly less relative proportions of quartz and more muscovite and chlorite with minor amounts of mixed-layer illite-smectite, gypsum, kaolinite and biotite. Figure 4.11 shows the relative proportions of the minerals identified in the soils overlying the Anson Formation. The samples associated with erosional sediments for the most part show higher proportions of quartz content despite coming from locations that overlie the Byng Volcanics. All but one show minor amounts of minerals that are also in the Byng Volcanics soils while the exception closely resembles the proportions of Byng Volcanics soils. Figure 4.12 shows the relative proportion of the identified minerals within these erosional sediments. A comparison of two soil samples taken from the same sample location is displayed in Figure 4.13.

Figure 4.9 mineralogy of the soils overlying the Byng Volcanics at five different field locations.
Figure 4.10 Mineralogy of soils overlying the Mullions Range Volcanics at four different field locations.

Figure 4.11 Mineralogy of soils overlying the Anson Formation at six different field locations.
Figure 4.12 Mineralogy of erosional sediment at four field locations along erosional channels and Black Bulga Creek.

Figure 4.13 Comparison of two separated soil samples from the same field location.
4.3.1.2 Profile Samples

Only profile MBP2 produced enough samples to be analysed by XRD as samples were collected in the field based on the change in copper content and this profile produced the most varying copper concentrations as well as reaching a significant depth. Other profiles either did not vary considerably in their copper concentrations or were not able to reach significant depths. The samples of this profile were also separated into their sand and silt/clay fractions. Figures 4.14 and 4.15 show the change in mineralogy with the depth in the profile for the sand and silt/clay fractions respectively. A distinct change in the proportions of the mineralogy in this profile occurs between 50 cm and 115 cm depth in the profile although the type of minerals present appears to remain fairly similar. The main minerals being quartz, hornblende, cordierite, actinolite, tremolite, albite and vermiculite.

![XRD mineralogy of profile MBP2 sand fraction](image)

Figure 4.14 Mineralogy of the sand fraction with depth of samples from profile MBP2.
Figure 4.15 Mineralogy of the silt/clay fraction with depth of samples from profile MBP2.

4.4 Organic matter content
Organic matter content as measured by loss on ignition separated into the surface soil fractions and the profile fractions. This is an estimation of organic carbon content as it may be possible that carbonates were present in the soil samples although these were not identified to any great extent by the XRD analysis. Organic carbon content may also have been over estimated due to loss of water from clay minerals that may have been trapped within the layers of clay particles. Table 4.4 gives the average organic carbon content as a percentage for the different surface soils based on the geology they overlie. Table 4.5 gives the average values of organic carbon content as a percentage for profile MBP2 separated between the sand and silt/clay fractions.

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Std deviation</th>
<th>Median</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total</strong></td>
<td>10.44</td>
<td>3.52</td>
<td>10.21</td>
<td>5.30-19.84</td>
</tr>
<tr>
<td><strong>Byng</strong></td>
<td>9.33</td>
<td>2.51</td>
<td>9.33</td>
<td>5.75-13.45</td>
</tr>
<tr>
<td><strong>Mullions</strong></td>
<td>11.03</td>
<td>6.31</td>
<td>9.49</td>
<td>5.30-19.84</td>
</tr>
<tr>
<td><strong>Anson</strong></td>
<td>11.72</td>
<td>2.49</td>
<td>12.26</td>
<td>7.24-13.91</td>
</tr>
</tbody>
</table>

Table 4.4 Organic carbon content in soils overlying the different geology.
Table 4.5 Organic carbon content in profile MBP2.

4.5 Estimated cation exchange capacity (CEC)
Cation exchange capacity for the different soils was estimated by combining the average values of CEC, as listed in literature, for the proportions of the different clay minerals and organic matter in each sample. As organic matter is probably overestimated and contributes a high CEC, the soil CEC is likely to be overestimated as well. Averaged results for the estimated CEC of the soils overlying the different geology are listed in Table 4.6 while the CEC values for profile MBP2 are displayed in Figure 4.16.

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Std Dev</th>
<th>Median</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>6.26</td>
<td>1.65</td>
<td>6.46</td>
<td>4.44-8.00</td>
</tr>
<tr>
<td>Sand</td>
<td>4.74</td>
<td>0.50</td>
<td>4.54</td>
<td>4.44-5.64</td>
</tr>
<tr>
<td>Silt</td>
<td>7.77</td>
<td>0.29</td>
<td>7.84</td>
<td>7.29-8.00</td>
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</tbody>
</table>

Table 4.6 CEC of the soils overlying the different geology.

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Std Dev</th>
<th>Median</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
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<td>8.41</td>
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<tr>
<td>Byng</td>
<td>21.58</td>
<td>6.17</td>
<td>21.41</td>
<td>12.34-31.73</td>
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<tr>
<td>Mullions</td>
<td>24.64</td>
<td>13.23</td>
<td>21.58</td>
<td>12.35-43.03</td>
</tr>
<tr>
<td>Anson</td>
<td>29.30</td>
<td>6.81</td>
<td>30.09</td>
<td>17.64-37.92</td>
</tr>
</tbody>
</table>

Figure 4.16 CEC change with depth of profile MBP2.
4.6 Soil pH

The pH results of the less than 2mm fraction of surface soil samples collected, in both water and calcium chloride solution, are as shown in Table 4.7 and Table 4.8 with the raw data displayed in Appendix C1. A map of surface soil pH was generated in ArcGIS using the IDW method, though due to the small number of data points available the model is only plausible close to these points. The pH of the unseparated, less than 2mm fractions, of profile samples were measured alongside the surface samples with the results of profile MBP2 displayed in Figure 4.20 and full results in Appendix C1.

Figure 4.17 Show the correlation of soil pH values between analysis done in water and CaCl$_2$ solution.

Figures 4.18 and 4.19 show the maps generated based on the surface soil pH values.

Figure 4.20 shows the pH changes with depth based on soil samples from profile MBP2 for both water and calcium chloride solution.

Table 4.7 shows the pH averages, standard deviations, medians and ranges based on the entire surface soil samples analysed and then separating these into particular areas of the field such as slag heap, mine site and the remaining soil samples.

Table 4.8 shows the pH averages, standard deviations, medians and ranges based on the results separated by the type of geology the soil is believed to be situated above.

![Correlation between soil pH in water and soil pH in calcium chloride solution.](image)

Figure 4.17 Correlation of the pH values for the two analyses.
Soil pH in deionised water

Figure 4.18 Soil in water pH map of the abandoned Mount Bulga Copper mine.
Figure 4.19 Soil in calcium chloride solution pH map of the abandoned Mount Bulga Copper mine.
Figure 4.20 Measured pH of profile MBP2.

<table>
<thead>
<tr>
<th>pH in water</th>
<th>Average</th>
<th>Std deviation</th>
<th>Median</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total sample locations</td>
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<td>3.64-7.96</td>
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<tr>
<td>Slag heap samples</td>
<td>5.10</td>
<td>0.894</td>
<td>5.05</td>
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<tr>
<td>Mine site samples</td>
<td>5.59</td>
<td>1.23</td>
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<td>3.95-7.96</td>
</tr>
<tr>
<td>Other sample locations</td>
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<td>4.18-7.03</td>
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<td>pH in calcium chloride</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total sample locations</td>
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<td>3.47-7.27</td>
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<td>Slag heap samples</td>
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<td>4.70</td>
<td>3.87-7.24</td>
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<td>Other sample locations</td>
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<td>0.678</td>
<td>4.51</td>
<td>3.62-6.57</td>
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</table>

Table 4.7 pH results for surface soils based on location.
<table>
<thead>
<tr>
<th>pH in water</th>
<th>Average</th>
<th>Std deviation</th>
<th>Median</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Byng Volcanics</td>
<td>5.55</td>
<td>0.573</td>
<td>5.37</td>
<td>4.62-7.03</td>
</tr>
<tr>
<td>Mullions Range Volcanics</td>
<td>4.80</td>
<td>0.317</td>
<td>4.87</td>
<td>4.23-5.20</td>
</tr>
<tr>
<td>Anson Formation</td>
<td>4.99</td>
<td>0.631</td>
<td>4.75</td>
<td>4.18-6.48</td>
</tr>
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<td>pH in calcium chloride</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Byng Volcanics</td>
<td>4.93</td>
<td>0.599</td>
<td>4.65</td>
<td>4.17-6.57</td>
</tr>
<tr>
<td>Mullions Range Volcanics</td>
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<td>0.218</td>
<td>4.04</td>
<td>3.65-4.20</td>
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<tr>
<td>Anson Formation</td>
<td>4.33</td>
<td>0.646</td>
<td>4.04</td>
<td>3.62-5.69</td>
</tr>
</tbody>
</table>

Table 4.8 pH results for surface soils based on underlying geology.
4.7 Total Metals by XRF
4.7.1 Portable XRF Field
Total metal content of soil and sediment at field sample locations (Figure 4.21) was carried out using the Niton XL3t portable handheld XRF analyser. Full results of this field analysis are displayed in Appendix A1.

Figure 4.21 XRF field sampling locations.
4.7.1.1 Transects
XRF analysis along transects with GPS coordinates recorded for each sample location allowed the distribution of metals in the surface soil to be mapped over the extent of the field. Maps were created in ArcMap 10.2 where the sampled points were used to interpolate a surface based on the inverse distance weighted (IDW) method and the total specific metals content at each point. Due to the abandoned mine sites and smelter dominating the maps some maps were created by removing the influence of those sites and by selecting points based off a limiting value of the metals concentration and then this was used in the IDW calculation. All maps are displayed in Appendix A6.

Figure 4.22 shows the distribution of copper in ppm over the extent of the field showing the influence of the mine sites in the centre and north and slag heap in the south.

Figure 4.23 shows the distribution of copper about the abandoned mine site and in relation to the slope of the land.

Figure 4.24 shows the distribution of copper in ppm with the influence of the mine sites and slag heap removed and any values above 75 ppm. 75ppm was chosen as it appears to be the lowest range and possibly background in the first map.

Figure 4.25 shows the distribution of zinc in ppm over the extent of the field. The influence of the old mine sites can be seen in the north and the slag heap in the south.

Figure 4.26 shows the distribution of lead in ppm over the extent of the field.

As transects are 200 m apart, values away from points are likely artefacts of the interpolation model and become increasingly unreliable. Also the model only displays values between the maximum and minimum recorded values and so there may well be places with metal contents above the maximum value stated on the map legends.
Figure 4.22 XRF Cu distribution at abandoned Mount Bulga Copper Mine.
Figure 4.23 Copper distribution about the abandoned mine site. Contour data from LPI NSW BTDB 2012, copyright © NSW Government. Land and Property Information (LPI) 2012.
Figure 4.24 XRF Cu <75 ppm distribution about the abandoned Mount Bulga Copper Mine.
Soil XRF analysis Zinc

Figure 4.25 XRF Zn distribution at the abandoned Mount Bulga Copper Mine.
Soil XRF analysis Lead

Figure 4.26 XRF Pb distribution at the abandoned Mount Bulga Copper Mine.
4.7.1.2 Profiles
Total metal analysis using the handheld XRF was also carried out on a number of profiles at locations shown in Figure 4.27. This was done to determine the change with depth of metal concentrations which may also potentially indicate the mobility of different metals. Results for profile MBP2 are shown while the full results are displayed in Appendix A3.

Figures 4.28 through to 4.32 show the concentration with depth of various metals in sediment from profile MBP2.

![Figure 4.27 Site locations of soil/sediment profiles.](image)
Figure 4.28 XRF Cu concentration with depth profile MBP2.

Figure 4.29 XRF Zn concentration with depth profile MBP2.
Figure 4.30 XRF Pb concentration with depth profile MBP2.

Figure 4.31 XRF Ni concentration with depth profile MBP2.
4.7.2 Laboratory XRF and Portable XRF University
A subset of collected soil samples representing locations over different geology as well as sediment samples from near the creek, erosional channel and profile MBP2 were chosen to be analysed by the Laboratory XRF to compare the results from the handheld portable XRF analyser. Correlation curves were constructed between the handheld portable XRF field results and the laboratory results. This was also done with the handheld portable XRF results obtained from the samples again back at the university after the profile samples had been separated into the sand and silt/clay fractions. Unfortunately due to the use of the chrome ring mill during crushing, half the samples could not be compared using the elements chromium, nickel, and vanadium.

Figures 4.33 through to 4.35 show the correlation curves of copper for the portable handheld XRF analyser and the laboratory XRF instrument, the difference between them is that the first is based on portable XRF data gained after some samples had been separated and all had been crushed at the university, the second is based on portable XRF data gained in the field, and the third is based on just the crushed but unseparated samples to compare to the same set of samples from the field.
Figure 4.33 XRF correlation curve for Cu based on separated and crushed samples.

Figure 4.34 XRF correlation curve for Cu between laboratory results and field results.

Figure 4.35 XRF correlation curve for Cu based on unseparated but crushed samples.
4.8 EDTA Extractable Metals by ICP-MS

4.8.1 Transect Samples

The results of the 0.05M EDTA metal extractions of the surface soil transect samples were compared to the handheld XRF measured total metal concentrations. The results for copper and lead, shown in Figures 4.36 and 4.37, give a strong positive correlation showing that extractable copper and lead increased with the increase in total copper and lead. Chromium shows only a slight positive correlation (Figure 4.38), while nickel appears to have no correlation (Figure 4.39). The slopes of the graphs would seem to suggest for these samples that copper is the most mobile relative to the total amount in the sample followed by lead, then nickel and then chromium. Unfortunately arsenic and zinc were not detected in many samples at the dilutions used and so were not able to be compared meaningfully with the XRF values.

Table 4.9 shows the average results for the mobility of the metals copper, lead, chromium and zinc as a percentage of the total XRF measured amounts. These results would seem to suggest that the average mobility of these elements follows Cu>Pb~Ni>Cr.

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Std deviation</th>
<th>Median</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Copper</td>
<td>35.57</td>
<td>23.05</td>
<td>32.37</td>
<td>8.00-84.53</td>
</tr>
<tr>
<td>% Lead</td>
<td>20.27</td>
<td>10.22</td>
<td>17.90</td>
<td>4.96-40.97</td>
</tr>
<tr>
<td>% Chromium</td>
<td>0.83</td>
<td>0.76</td>
<td>0.63</td>
<td>0.09-3.55</td>
</tr>
<tr>
<td>% Nickel</td>
<td>20.32</td>
<td>18.86</td>
<td>15.29</td>
<td>1.90-91.86</td>
</tr>
</tbody>
</table>

Table 4.9 Average results for mobile metals as a percentage of the total measured amount.

Figure 4.36 Correlation between mobile Cu and total Cu.
Figure 4.37 Correlation between mobile Pb and total Pb.

Figure 4.38 Correlation between mobile Cr and total Cr.

Figure 4.39 Correlation between mobile Ni and total Ni.
4.8.2 Profile Samples

Figures 4.40 through to 4.43 show the mobility of copper, lead, nickel and chromium in relation to their total XRF concentrations for the grain size separated samples of profile MBP2. All figures show the trend of decreasing mobility with depth. Copper and lead once again show the relationship of increasing mobility concentrations with increasing total concentrations, though copper appears to be more mobile in the silt/clay fraction than the sand fraction while lead is the opposite. Nickel and chromium appear to show a decreasing mobility concentration with increasing total XRF concentrations. Nickel, like lead, appears be more mobile in the sand fraction while chromium is slightly more mobile in the silt/clay fraction.

![Copper mobility in relation to total copper from profile MBP2.](image)

Figure 4.40 Mobile Cu compared with total Cu in the sand and silt/clay fractions of profile MBP2.

![Lead mobility in relation to total lead from profile MBP2.](image)

Figure 4.41 Mobile Pb compared with total Pb in the sand and silt/clay fractions of profile MBP2.
4.8.3 Mobility and mineralogy

Total concentrations and mobile concentrations of the metals copper, lead, chromium and nickel were plotted against the proportions of individual minerals identified by XRD for all samples, as were the mobility concentrations as a percentage of total XRF concentrations. This was done to see if there may be a relationship between particular minerals and the potential mobility of metals within the soil. Figures 4.44 and 4.45 show an increasingly mobile trend for copper and lead when the proportion of quartz increases. When the proportion of hornblende increases in the soil the opposite is seen for copper and lead as seen in Figures 4.46 and 4.47. Similar trends for copper and lead are seen with the minerals actinolite, tremolite, cordierite and vermiculite. These trends are not seen or obvious with
nickel or chromium but they both show a decrease in total concentrations as the proportion of quartz increases as seen in Figures 4.48 and 4.49. The opposite is seen in Figures 4.50 and 4.51 where the total concentrations of chromium and nickel increase with the increasing proportion of hornblende. This also occurs to some extent for chromium and nickel with the minerals tremolite, actinolite, cordierite and vermiculite.

![Figure 4.44 Increasing Cu mobility with increasing proportion of quartz.](image1)

![Figure 4.45 Increasing Pb mobility with increasing proportion of quartz.](image2)
Figure 4.46 Decreasing Cu mobility with increasing proportion of hornblende.

Figure 4.47 Decreasing Pb mobility with increasing proportion of hornblende.

Figure 4.48 Decreasing total Cr with the increase in the proportion of quartz.
Figure 4.49 Decreasing total Ni with the increase in the proportion of quartz.

Figure 4.50 Increasing total Cr with the increase in the proportion of hornblende.

Figure 4.51 Increasing total Ni with the increase in the proportion of hornblende.
Chapter 5: Discussion

5.1 Mineralogy of soils
The major minerals identified using XRD for soils overlying the Byng Volcanics were found to be tremolite, hornblende, cordierite, actinolite and quartz. Of these minerals all besides hornblende have been mentioned in the literature (Pogson and Watkins 1998) to be related to the greenschist altered Byng Volcanics. Other minerals present in trace amounts are also mentioned such as pumpellyite, chlorite and albite. Minerals mentioned that were not identified by XRD were epidote, augite and olivine. The proportion of hornblende identified in the soil, which is a total of hornblende and pargasite, may possibly be explained by a slightly higher P-T regime locally, compared to the region, which would have allowed the formation of hornblende in the series actinolite-hornblende-pargasitic hornblende-pargasite (Deer et al. 1992). Other possible pathways for the formation of hornblende is that they may form from metamorphic alteration with dolomitic limestones or that they can form as secondary minerals from pyroxenes (Deer et al. 1992). Although not detected in the Byng Volcanics soil samples, augite may be responsible for the appearance of secondary hornblende or tremolite. A further possibility that may support the occurrence of hornblende is the amount of vermiculite found in profile MBP2 which may be the result of weathered hornblende (Weaver 1958, Tomita et al. 1970), however the abundance of vermiculite may have been overestimated by the XRD analysis due to the way it may have sat flat against the glass window of the slide. Either way there appears to be a positive correlation between hornblende and vermiculite suggesting they may be related to each other, though this may also mean they are just related to the same soil and parent material. Epidote was not identified by the XRD analysis though clinozoisite is, which is in the epidote group and is the monoclinic form of zoisite and iron-absent form of epidote (Deer et al. 1992).

The major minerals identified by the XRD analysis for the soils believed to overlie the Mullions Range Volcanics shows that the major mineral in these soils is quartz. Other minerals found in smaller proportions are chlorite, biotite, mixed-layer illite-smectite, muscovite and hornblende. Thin section analysis of the Mullions Range Volcanics identified phenocrysts of quartz and albite with some minor biotite and muscovite. According to Pogson and Watkins (1998) the Mullions Range Volcanics just east of Orange contain phenocrysts of quartz, feldspars, biotite and cordierite while metamorphism formed epidote, biotite, chlorite and clinozoisite. The XRD analysis combined with the thin section analysis agree with the literature for most of the minerals, though cordierite and epidote were not identified. The appearance of a minor amount of hornblende again may be contamination from the Byng Volcanics or as a result of metamorphism again.
As with the Mullions Range Volcanics the XRD measured mineralogy of the Anson Formation shows a higher proportion of quartz relative to all other minerals. Other major or common minerals were muscovite, chlorite, mixed-layer illite-smectite, biotite, gypsum, kaolin and hornblende again. The mineralogy of the Anson Formation is split between the upper and lower parts of the sequence, with the lower conglomerate sequence showing similar mineralogy to the Byng Volcanics, while the upper sequence is related to the felsic lavas and volcaniclastics similar in mineralogy to the Mullions Range Volcanics (Pogson and Watkins 1998). The soils believed to overlie the Anson Formation probably overlie the upper part of the formation due to the rock samples taken from these areas lacking any conglomerate. This would be consistent with the description provided by Pogson and Watkins (1998) with the occurrence of quartz and chlorite, while sericite could account for the muscovite and mixed-layer illite-smectite. According to Deer et al. (1992) the presence of kaolin and illite may be explained by the weathering or hydrothermal alteration of feldspars and muscovite following the equation from feldspar.

\[
2KA\text{Li}_3\text{Si}_5\text{O}_8 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4\text{SiO}_2 + 2\text{K(OH)}
\]

The potassium may then be either leached away, or if not lost, illite is formed instead. Gypsum mainly occurs with sedimentary rocks of shales, claystones and limestones as well as evaporites so its presence associated with the Anson Formation is not surprising but it may also be a result of sulfuric acid, formed by the oxidation or weathering of sulfides, reacting with calcium in rocks and soils (Deer et al. 1992).

### 5.2 Distribution of metals

The geochemistry of the soils about the abandoned Mount Bulga Copper Mine as measured by XRF are highly influenced by the parent rock material underlying them. This is clearly seen in the maps that were generated by interpolating a surface based on the XRF measurements for a range of elements. Soils situated above and about the mafic Byng Volcanics generally have higher concentrations of the siderophile and chalcophile elements such as chromium, nickel, strontium, scandium, manganese, iron, calcium, copper and zinc. Soils situated above and about the Anson Formation and the felsic Mullions Range Volcanics tend to show higher concentrations of lithophile elements such as thorium, potassium and rubidium. The metal content of outcrop samples as measured by the handheld XRF show higher concentrations of copper, chromium, nickel, calcium, iron, strontium and manganese in the Byng Volcanics than in the Anson Formation or Mullions Range Volcanics, which closely agrees with the metal content of soils believed to overlie these units as seen in the maps. The higher concentrations of rubidium, thorium and potassium in
soils overlying the Mullions Range Volcanics and the Anson Formation compared to the Byng Volcanics are matched in the outcrop samples. The Anson Formation outcrop samples appear to show slightly elevated levels of lead and zinc in relation to the Mullions Range Volcanics and the Byng Volcanics, this could be related to the volcanic hosted massive sulfide deposit being contained within this unit and the higher values are a result of these two metals being spread beyond the deposit within the sediments. However the higher concentrations may also be the result of surface contamination of the rock and weathering.

The geochemistry of the soils show a definite separation between the mafic Byng Volcanics and the felsic Mullions Range Volcanics with a line of separation trending in a north-westerly direction. Along this separation line were found the highest values of sulfur and this probably marks the location of the shear zone that the sulfide mineralisation mined at Mount Bulga is situated within. Also at the northern end of this shear zone iron concentrations are raised along this line but are low on either side of it. This is probably most related to the weathered gossanous capping formed at the surface of the shear zone as a result of oxidation and leaching of the sulfide mineralisation. Large concentrations of copper, zinc and lead were found in the shear zone gossan sample. The southern part of the shear zone appears to be dominated by higher concentrations of copper with minor zinc and very low lead, while the middle of the shear zone is dominated by higher concentrations of zinc with copper and the most northern part of the shear zone is mostly higher concentrations of lead with minor zinc and low copper.

This volcanic hosted massive sulfide deposit is believed to have been remobilised into the shear zone (Kennedy and Weber 1965). This must have involved hydrothermal fluids in order to have dissolved and then reprecipitated these elements as sulfides within the shear zone. Following the shear zone to the most southern part of the map it comes into contact with an ultramafic intrusion which may have been related to the event responsible for providing the heat source required to generate the hydrothermal fluids capable of mobilising the metals along the shear zone. This may also explain the zonation within the shear zone of copper, lead and zinc as a function of decreasing temperature with distance from this intrusion. Typically copper will precipitate at higher temperatures than zinc or lead (Trefry et al. 1994, Metz and Trefry 2000), where higher temperatures would be closer to the heat source.

The abandoned mine sites and slag heap show the highest concentrations of copper, lead and zinc as well as arsenic and include the highest values of iron and sulfur. Due to these large concentrations it is likely that these hold the highest potential for metal mobility as not
only do they contain the highest concentrations but they also lack vegetation cover and for the most part have higher proportions of sand and lower proportions of organic matter. The map of copper concentrations about the mine site in regards to slope shows a trend of copper concentrations flowing down hill to either side of the earthen embankments built to direct this drainage to the limestone drainage channels. This would that copper at least is being mobilised off the mine site down this drainage channel. A map of the slag heap (Appendix A6) shows some slight elevations of copper concentration to the east, while the west side is fairly low, suggesting this may be wind deposited by westerly winds.

5.3 Mobility
5.3.1 Transects
For the most part copper lead and chromium showed an increase in mobility with an increase in total concentrations, while nickel did not appear to show any correlation. Copper and lead also did not appear to show any trend when plotted against different mineral fractions. However when these elements were plotted with their mobility concentrations as a percentage of total concentrations in relation to the different minerals some trends were observed. When plotted against quartz there is a definite trend for both copper and lead showing an increase in the proportion that is mobile with an increase in the proportion of quartz. When plotted against hornblende, actinolite, cordierite, and vermiculite the opposite is seen with a decrease in the mobile proportion while the mineral proportions increased. This relationship might be explained by the possible cation exchange capacity of the soil as the increase in the dominance of quartz would have the effect of lowering this leaving less sights for copper and lead to bind to while any samples that contained high quartz but low mobility may be due to the metals being locked up in minerals or immobile precipitates. Another explanation is that there appears to be a relation to pH and certain minerals, with moderate to weak positive correlations of pH with the minerals vermiculite, magnetite, albite, hornblende, dolomite and actinolite, while there is moderate to weak negative correlations with quartz chlorite, kaolin, antigorite, pyrrhotite and illite. The combination of low CEC and low pH would probably promote metal mobility from easily exchangeable sites and dissolved solids which would agree with what is seen with copper and lead mobility with quartz, while higher CEC of vermiculite with increasing pH would favour precipitation and adsorption to exchange sites. Chromium and nickel both show decreasing total concentrations with increasing quartz and chlorite content and increasing total concentrations with increasing hornblende, actinolite, tremolite, cordierite and vermiculite probably reflecting the source rock the metals are associated with. Both chromium and nickel mobility appear not to be related to their total concentrations suggesting most of the
metals are locked up in mineral or insoluble phases. The percent mobility of both these elements show slight similarities to copper and lead except for hornblende and quartz.

5.3.2 Profiles: Copper and Lead
Copper concentrations for the most part remained fairly low in the profiles investigated but where the concentrations were raised they tended to be high at the surface and decrease towards the base of the profile. Lead remained fairly consistent throughout all profiles investigated remaining fairly low in concentration with the occasional small spike before returning to the concentration range 10-20 ppm. Zinc was fairly consistent through most of the profiles ranging from about 30-60 ppm, though profile MBP1 showed a spike at about 2 metres down the stream bank while profiles MBP2 and MBP4 are high at the surface but quickly fall back to the afore mentioned concentration range at depth. These metals are likely high in concentration at the surface as they are a result of the weathering of sulfides containing these elements which may have then become immobilised by adsorbing to clay minerals or iron and manganese oxyhydroxides. If this is the case it may explain the lower pH at the surface of profile MBP2 with the breakdown of sulfides creating sulfuric acid. The mobility of both copper and lead in profile MBP2 for the most part show an increase in the mobility concentrations with an increase in total concentrations which is opposite to what is seen with the nickel and chromium concentrations. All four metals show a decrease in mobility with a slight increase in pH and for the most part a decrease in mobility with depth, suggesting pH plays an important role in metal mobility, at least, in profile MBP2. This may also possibly be explained by the effects of Eh as, with depth, reducing conditions are more likely and so particular precipitates, or adsorbed species, that were difficult to mobilise may be dominant. Unfortunately Eh was not measured and so this relationship can only be assumed for this situation. The difference in mobility with depth may also be explained by the change in mineralogy also, with a larger relative proportion of quartz at the surface the cation exchange capacity would likely be lower at the surface and increase with depth with the increase of clay minerals. This is what was observed in profile MBP2 with the estimated CEC increasing with depth especially in the silt/clay fraction.

5.3.3 Profiles: Chromium and nickel
The distribution of chromium and nickel within the profile samples for the most part show an increase in concentrations with depth. This distribution of chromium and nickel is most likely due to an increase in the proportion of particular silicates or insoluble minerals that contain these elements. In profile MBP2, measured mobile chromium concentrations appear
to decrease with increasing total chromium concentrations and the mobile concentration is significantly lower than the total concentration suggesting that chromium is related to insoluble or silicate phases. Nickel follows a similar pattern but is much more mobile relative to total concentrations, especially in the sand fraction. Although this pattern may possibly be explained by pH as it was measured at close to a pH of 5 at the surface and then steadily increased with depth towards neutral pH which would promote precipitation at depth with the formation of metal hydroxides. Profile MBP2 also shows a change in mineralogy in both the sand and silt/clay fractions with depth with the increase in the proportions of the minerals cordierite, actinolite, vermiculite, hornblende and antigorite. While these minerals are also in small quantities near the surface the major mineral at the surface is quartz. Plots of the total and mobile concentrations of nickel and chromium against the relative proportions of quartz in all analysed soil and profile samples show that total nickel and chromium decrease with increasing proportions of quartz while the mobile concentration for both elements tends to stay fairly low in proportion to total concentrations. The opposite occurs with the minerals hornblende, cordierite, actinolite and vermiculite, with total concentrations of nickel and chromium increasing with increasing concentrations of these minerals. This, along with the low mobility in relation to the total concentrations, would again suggest that chromium and nickel are bound in insoluble and silicate phases, either within or closely related to the minerals hornblende, cordierite, actinolite and vermiculite or some other unidentified mineral. In most soils chromium is predominantly in the Cr$^{3+}$ state as part of the oxide Cr$_2$O$_3$ which is insoluble between the pH range of 5 to 13.5 and Eh range of +0.8V to -0.75V (Motzer 2004). The pH values for profile MBP2 in water are all within this range and although Eh was not measured the increasing depth would likely favour reducing conditions further favouring Cr$_2$O$_3$. The oxidation of Cr$^{3+}$ to the more mobile Cr$^{6+}$ may occur under more oxidative conditions such as near the surface, which would agree with the increased mobility near the surface in profile MBP2, however the occurrence of this would likely be minimal as the oxidation reaction typically requires the presence of manganese oxides acting as the oxidant and for chromium to be mobile in the first place in order to be available for reaction while any chromium that does get oxidised to Cr$^{6+}$ is quickly reduced by organic matter back to Cr$^{3+}$ (Zayed and Terry 2003). This low mobility of chromium as seen in the EDTA extraction on all analysed samples would appear to agree with chromium being fairly immobile and that chromium is likely associated with mineral and insoluble phases. An explanation for the higher concentration of chromium with depth may be that this marks an
old residual soil surface as residual soils tend to show similar chromium concentrations to the parent rock material (Motzer 2004). The average concentration measured by XRF for an outcrop of Byng Volcanics was 906 ppm of chromium compared to a similar amount at about 150 cm depth in the profile sample, although concentrations begin to drop again afterwards. If acid mine drainage was evident at Mount Bulga and the pH was significantly lower than measured, then the mobility of Cr$^{3+}$ would likely be increased allowing the formation of Cr$^{6+}$ under oxidative conditions and the occurrence of manganese oxides (Zayed and Terry 2003). This may be offset though by the occurrence of clay minerals as Cr$^{6+}$ and Cr$^{3+}$ are strongly held by clay minerals and this increases with the lowering of pH for Cr$^{6+}$ (Zayed and Terry 2003).

Nickel is mainly found in highest concentrations in ultramafic rocks followed by mafic rocks where nickel commonly can substitute for iron or magnesium in minerals such as chlorite, serpentine, pyroxene and olivine (Massoura et al. 2006). Although antigorite, a serpentine mineral, is present in profile MBP2 and so is chlorite, nickel conceivably could also be present in the amphiboles hornblende and actinolite as well as in vermiculite as these minerals also contain magnesium and iron for which it could substitute. According to Chardot et al. (2007) nickel mobility depends mostly on the soil pH. While nickel is predominantly held on amorphous iron oxides and high charge clay minerals as pH increases, though in highly weathered soils nickel mobility will be low due to nickel being incorporated into the crystal lattice of well crystallised iron oxides such as goethite. The high mobility but lower total nickel concentration and low mobility but higher total nickel concentration pattern observed in the sand fraction of profile MBP2, with the higher mobility towards the surface of the profile, probably suggests that the nickel concentrations near the surface are as a result of the weathering of nickel bearing mineral phases, while the change in mobility is probably due to pH changes. The higher proportions of quartz near the surface could explain the lower total nickel concentrations as this would promote leaching of nickel due to the low cation exchange capacity of quartz and lower pH values. The high total nickel concentrations at depth but low mobility would seem to suggest nickel here is predominantly held in mineral phases.

5.4 Acid mine drainage.

5.4.1 pH

At Mount Bulga the main areas that would likely contribute to acid mine drainage would be the old mine shafts and surrounds where ore heaps and spoil would likely have been placed. The site where the smelter was situated would be another possible source of acidity as ore
heaps would have been deposited nearby and slag from the smelter dumped. At the old mine workings, there appear to be no significant ore or mine spoils, though some ore material is lying about the Mount Bulga Copper Mine site. There is a significant amount of slag at the smelter site but again any ore material has either been removed or spread out. There was no identification of any tailings.

The pH measured at the centre of the abandoned mine site at Mount Bulga was fairly close to neutral. This may be a result of the remediation efforts currently ongoing there. However surrounding the mine site, several of the samples become moderately acidic and the mine site is lacking in significant vegetation. This is probably related to sulfides spread about the surface breaking down, but may also be due to iron and manganese precipitating producing further acidity. There are limestone drains emplaced downhill from the mine site as part of the remediation efforts in order to neutralise any acidity, but these do not appear to be significantly coated in any iron and so may suggest no significant acid mine drainage. Malachite precipitation was observed draining from out of the soil covering the old mine shaft (Figure 5.1) which may suggest a source of carbonate within the remediated mine shaft possibly explaining the almost neutral pH over the mine site and high calcium values measured by XRF. Downslope from the mine site, following the drainage channel, pH appears to be lower at points in this direction, although there are relatively few points so a good indication of if pH is really being affected by runoff from the mine site is not absolutely determined.

Figure 5.1 Possibly malachite precipitating as water drains from the mine site.
The pH measured about the slag heap shows the area just north of it to be strongly acidic. This is probably the location ore from the mine was transported to and dumped waiting to be put through the smelter. Therefore this acidity is likely due to the breakdown of sulfide materials. This area is also lacking in any vegetation probably as a result of the acidity of this soil which extends as a strip from the slag heap towards the mine site. Directly below the slag heap the soil becomes moderately acidic before increasing and becoming more neutral near the creek. This area is where any water passing over and about the slag heap would drain through to reach Black Bulga Creek. This is also where profiles MBP2 and MBP3 were situated which identified higher values of copper and zinc near the surface in MBP2 closer to the slag heap, while profile MBP3 identified low concentrations of these metals. This may suggest that although the metals appear to be mobile off the slag heap they are being retained in the soil as acidity is neutralised closer to the creek.

5.4.2 Estimated CEC
Particle size for all soils measured ranged from sandy loam to silt loam and silt with the vast majority being silt loams. This would suggest that these soils have a fairly low cation exchange capacity. Silt loams tend to have cation exchange capacities of about 5-15 cmol(+)/kg which is lower than the amounts estimated from the combination of the organic matter and clay minerals identified by XRD. Soils above the Byng Volcanics averaged 21.58 cmol(+)/kg. Soils above the Mullions Range Volcanics averaged 24.64 cmol(+)/kg. Soils above the Anson Formation averaged 29.30 cmol(+)/kg. These slightly higher values estimated may be due to an overestimation of organic carbon content and specific clay minerals. The organic matter content may have been overestimated due to possible carbonate minerals present within the sample or water present within the layers of clay particles, which would have also been lost on ignition along with the organic carbon, resulting in a mass loss greater than the actual organic carbon mass. Not many samples though identified carbonates within the soil and for those that were identified they were usually low in proportion and included dolomite, some calcite, malachite and azurite. The CEC may well be higher than that estimated also as the CEC values, representing each clay mineral and organic matter, used average values gained from a text (VanLoon and Duffy 2010). The average estimated CEC values of soils overlying the Byng Volcanics and the Mullions Range Volcanics are similar while the average estimated CEC value of soils overlying the Anson Formation is higher. The higher CEC value for the Anson Formation is not surprising as this is a sedimentary unit which contains mainly siltstone where the samples were collected. These low CEC values estimated for the soils would seem to suggest that these soils would not be ideal for buffering any changes in pH that may occur
due to acid mine drainage, at least not at the surface. Profile MBP2 shows a trend of increasing estimated CEC with depth which is a result of the increase in clay minerals observed in this profile, particularly vermiculite. The increase in pH observed in this profile would probably also have the effect of increasing the CEC, though this is not taken into account when estimating the CEC. This possible increase in CEC with depth, combined with the increase in pH with depth, would help to retain any mobile elements as well as buffer any change in pH due to acid mine drainage.

5.5 Investigation Levels
Apart from arsenic, chromium and lead none of the other metals exceed total concentrations that would trigger an investigation into the potential hazard these metals may pose according to the ASC NEPM (2013) guidelines based on developed open space parkland. Even though there are one or two places where lead exceeds these concentrations, they are contained in or close to the shear zone within the pine forest, suggesting they may be natural concentrations for those areas. The chromium values also are based on the presence of chromium(VI) and as previously mentioned chromium(III) is more likely to be the species present. The measured mobility of chromium was fairly negligible and the high concentrations in the soil reflect similarly high concentrations with the Byng Volcanics outcrop sample. High arsenic values were contained within the northern part of the shear zone as well as at the mine site and slag heap. However away from these areas arsenic is rarely detected at significant levels. Only a small number of samples gave a mobile concentration above the detection limit for the dilutions used, which suggests that most of the arsenic may be locked up in iron hydroxides (Hamon et al. 2004).
Conclusions

At Mount Bulga past mining activities, focused on the remobilised volcanic hosted massive sulfide deposit in a shear zone, have brought sulfides to the surface where they have been able to oxidise, releasing large amounts of copper, zinc, lead and arsenic into the surrounding landscape. The oxidation of these sulfides has likely caused the strongly acidic soil immediately north of the slag heap and immediately south-west of the abandoned mine site. Moderate acidity located immediately south of the slag heap and following the drainage channel off the abandoned mine site would be as a result of acid mine drainage. The raise in pH to roughly neutral conditions at the creek from the acid drainage about the slag heap is due to the buffering capacity of the soil here, probably as a result of increased clay concentrations with depth of the soil. The effects of acid drainage from both the mine site and slag heap has resulted in soils that appear to be unable to sustain plant life and remain virtually bear of any vegetation allowing metals to be wind and water dispersed.

Although lead and arsenic had some samples above total guideline concentrations for outdoor space, these were either confined to the shear zone, slag heap, and mine site with no identified concentrations above the guidelines away from these areas. It is likely that the high concentrations of chromium and nickel are related to the local geology, particularly the Byng Volcanics. High concentrations in the surface soils of copper, lead and zinc are a result of the breakdown of sulfide material from the shear zone and have then probably adsorbed onto clay particles and iron or manganese hydroxides which have then been dispersed by either wind or water runoff.

Metal mobility down profile MBP2 was either a factor of CEC, pH or Eh or a combination of all of these. Metal concentrations in profile MBP2 were related to immobile phases with copper probably adsorbed to solid phases at the surface and chromium and nickel related to the underlying geology. Unfortunately it was not possible to determine the initiation of mining activities at Mount Bulga, although the change in mineralogy part way down profile MBP2 may be related in some way.
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