



Acidic Receiving Waters Impact on Metal Solubility from Conventionally Treated Mine Drainage

Master of Research - Environmental Sciences

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Statement of Originality

This work has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made in the thesis itself.

(Signed) _____

Date: 08/10/2017_____

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Abstract

Research, management and regulations surrounding acid mine drainage typically focuses on the composition of the drainage and treated discharge. Absent from applied and site based research, and consequently regulation, is how lime neutralised alkaline discharge behaves once discharged into naturally acidic streams. In effect, precipitated metals in the alkaline discharge and sediment, the result of lime treatment, are re-acidified as water returns to its naturally acidic state, causing the dissolution of metals into the environment. This is the case at Clarence Colliery, an underground coal mine located in a World Heritage listed area 100 km from Sydney. Total and dissolved metals in water and sediment were measured longitudinally downstream and sediment from the mine discharge was exposed to different pH (4-8) in extraction tests. Results revealed that remobilisation of metals commenced as soon as 200m downstream (pH change 8.05 to 7.75), with contamination extending 21km downstream. Metal solubility increased in sediments as pH returned to its natural acidic condition (pH 5). The study highlights the need for environmental regulators to assess metal remobilisation from conventional lime treatment systems and points to legacy contamination issues associated with metal rich sediments already located in stream.

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Introduction

Acid mine drainage (AMD) has the potential to cause significant environmental harm. AMD is formed due to chemical reactions between rocks containing sulphide minerals, water and oxygen. AMD can form sulfuric acid and dissolved Fe and if left untreated will cause significant environmental problems. AMD impacts the physio-chemical balance and ecology of the receiving waters through a reduction in pH, metal toxicity, elevated conductivity and sedimentation (Herlihy et al. 1990, Maltby and Booth 1991, Winterbourn and McDuffett 1996, Verb and Vis 2000, Cherry et al. 2001, DeNicola and Stapleton 2002, Freund and Petty 2007; Gaikwad et al., 2011; Gray, 1997).

For the coal industry, AMD is one of the major environmental problems associated with current and abandoned mines. The impacts of coal mine water including treated and untreated AMD discharge is an issue of global concern and has been relatively well studied, for example: Australia (Wright et al., 2017; Wright et al., 2015; Belmer et al., 2014; Phillip and Wright, 2015); New Zealand (Hugh et al., 2011; Winterbourn 1998; Gray and Harding 2012); USA (Maccausland and Mctammany, 2007; Verb and Vis 2000; Brake et al. 2001; Pond et al. 2008; Griffith et al. 2012); Brazil (Lattuada et al. 2009); UK (Younger, 2001, Jarvis and Younger 1997; Younger 2004; Johnson, 2004); and India (Sahoo et al., 2011).

As an area of international research, much of the focus from a science, regulatory and operational perspective has been orientated towards managing coal mine AMD and associated contaminants linked to surface and groundwater discharge. Less researched has been the implications of AMD on naturally acidic streams and the impacts of discharging treated, typically alkaline, mine wastewater. In particular it is now known what spatial and temporal effects treated AMD has on metal solubility within the stream environment as water and sediments naturally re-acidify.

Determining the potential solubility of metals from sediments is necessary if mining operations are to have a minimal environmental impact. Approximately 90% of metals end up bound in suspended particles or in the sediment (Zheng et al., 2008; Amin et al., 2009; Calmano, et al., 1993). Buffering capacity of the receiving environment will play a major role in determining if these bound-up metals will be released into the environment (Plumlee et al., 1999; Toyer and Main, 1981; Glass et al., 1982). While the effect of low pH waters on metal solubility in sediment has been well studied in lakes, reservoirs, estuarine and ocean sediments; these are reducing environments (Szarek-Gwiazda, 2014; Tack et al., 1996; Trefry and Metz, 1984). There is less research on the impact of mine waste water on naturally acidic and pristine freshwater waterways, which are oxidising and have low buffering capacity. Such systems present a dilemma to conventional lime based

precipitation treatments and standard regulatory regimes orientated around minimising the impacts of low pH and end of pipe treatment. Paradoxically, conventional treatment of AMD through conventional lime precipitation treatments may add to the environmental impact of mine wastewater on the natural environment through secondary solubility from acidic pH. Naturally acidic, oxidised and low buffering streams are present in many of the coal mining areas in NSW, specifically the western coalfields region surrounding Sydney.

As an industry in NSW coal mining is a major economic activity and produced 246.8 million tonnes of raw coal in 2015/16 (NSW Department of Industry, 2017). The NSW Environment Protection Authority (EPA) is the environmental regulator of coal mining in NSW and permits discharge of pollution into the environment through environmental pollution licences (EPL). The EPL and associated regulatory mechanisms of the EPA are used to manage the immediate and long term environmental impacts of this industry. In relation to AMD, this is of concern to the EPA, however less clear is how licenced discharges regulate pollutants where the natural geochemistry may cause secondary impacts on receiving waterbodies.

This study is based on Clarence Colliery in the Blue Mountains, NSW. The mine and its impacts on the Wollangambe River is one of the most studied (Wright et al., 2017; Belmer et al., 2014; NSW OEH, 2015; Cohen, 2002; Jones and Riley 1996; Jones and Eames, 1996) mine discharge sites in Australia. The headwater streams above the mine contain virtually untouched bushland providing a natural or reference condition from which to assess the impact of the mine. Other than a quarry adjacent to the Clarence Colliery, the mine is the only land use in the immediate catchment, having a notable impact on Wollangambe River up to 22km downstream. The mine is located adjacent to the Blue Mountains National Park, forming part of the Greater Blue Mountains World Heritage Area (GBMWhA). These characteristics enable a longitudinal and temporal study of the effect of this mine on the environment.

Past studies on the Clarence Colliery have focused on metals from the mine wastewater discharge and have reported elevated concentrations in the Wollangambe River water and sediment that have been attributed to an adverse impact on invertebrate population and abundance (Wright et al., 2017; Belmer et al., 2014; NSW OEH, 2015; Cohen, 2002; Jones and Riley 1996; Jones and Eames, 1996). To-date, neither research nor regulation has explored the impacts of the change in pH on the 'reservoir' of metals in the sediments discharged from the mine. Specifically, how treated wastewater with higher pH (pH 6.9-8.7, mean 7.9) slowly returns to its naturally acidic (pH 4.6-6, mean 5.5) state once the mine closes, in doing so, may cause metals to become soluble. This is an issue presently for the mine and critically, if not adequately regulated, has the potential to create a long-term legacy contamination issue for the Wollangambe River.

This study aims to determine the effect of solubility of metals from the sediments in the Wollangambe River from the Clarence Colliery. It will examine metal solubility at the point of discharge and how metal solubility may change as pH returns to its naturally acidic condition. The study undertakes a longitudinal analysis of sediment and water composition up and downstream of the Clarence Colliery discharge in the Wollangambe River and determines the solubility of different metals from the river sediment at different pH using extraction tests.

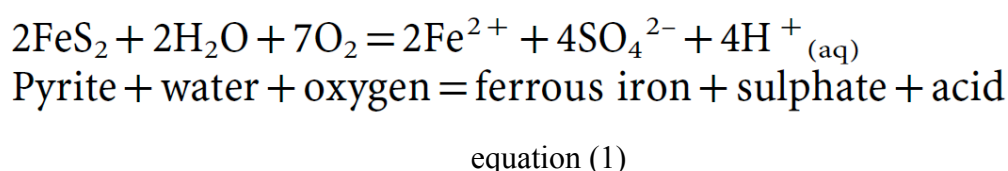
The motivations for this study are to identify current and emerging implications related to metal solubility, including potential post mine closure impacts on the Wollangambe River. It is designed to provide direction for alternative mine wastewater treatment and for future EPA pollution licensing. At a regional and international level, the study has utility as it offers insight into the potential for metal contamination of freshwater streams well downstream of licenced discharge points.

Literature Review

Acid Mine Drainage

Occurrence/Oxidation process

The geochemistry of AMD has been subject to numerous investigations: Alpers and Blowes (1994), Nordstrom and Alpers (1999), Frommichen et al (2004), Geldenhaus and Ball (1998), Jenkins et al (2000), Bachmann et al (2001), Holmstrom et al (2001), D.E.P (2002), Ehrlich (2004), Denimal et al (2005), Ackil and Koldas (2006) and Egiebor and Oni (2007). AMD is the result of the oxidation of Fe sulphide minerals when exposed to oxygen and water. Sulphide minerals are formed under reducing anoxic conditions. There is a variety of acid producing sulphides of which pyrite is the dominant sulphide responsible for acid generation. When exposed to oxygen and water (or oxygenated water) these minerals become unstable, oxidise, resulting in sulphuric acid production and ferrous Fe. (Eq 1.)



The acidic drainage leads to the mobilisation (leaching) of metal(oids) present in the ore, tailings, and waste rock such as As, Sb, Cu, Pb, Cd, Zn, Hg, Ag, Sn, Fe, Al, Mn, Tl, U, Th and W (Ashley et al., 2003, 2004; Modabberi et al., 2013). These metals may be brought into solution thereby contaminating surface and groundwater systems.

AMD Sources and Pathways

The generation, mobility, release and impacts of AMD is influenced by a combination of biological, physical and chemical factors. The environmental impact of AMD depends on the characteristics of the sources, pathways, and receiving environment (Figure 1A.). These sources, pathways and receiving environments vary based on the mine type, climate, commodity and mine phase (INAP, 2014). There are three important variables that influence AMD from the sources to the receiving environment: factors determining the rate of sulphide oxidation; factors modifying the composition of drainage in the mine waste; and factors modifying the composition of drainage once discharged from the facility by the receiving environment (Figure 1B.) (INAP, 2014)

(A)

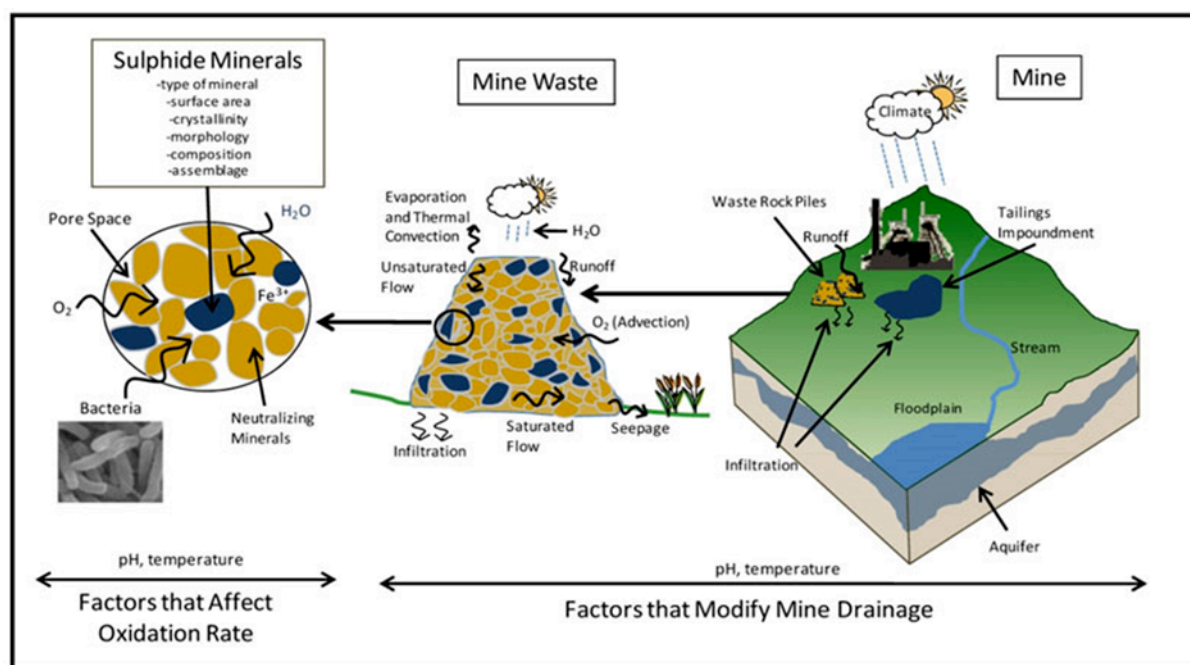
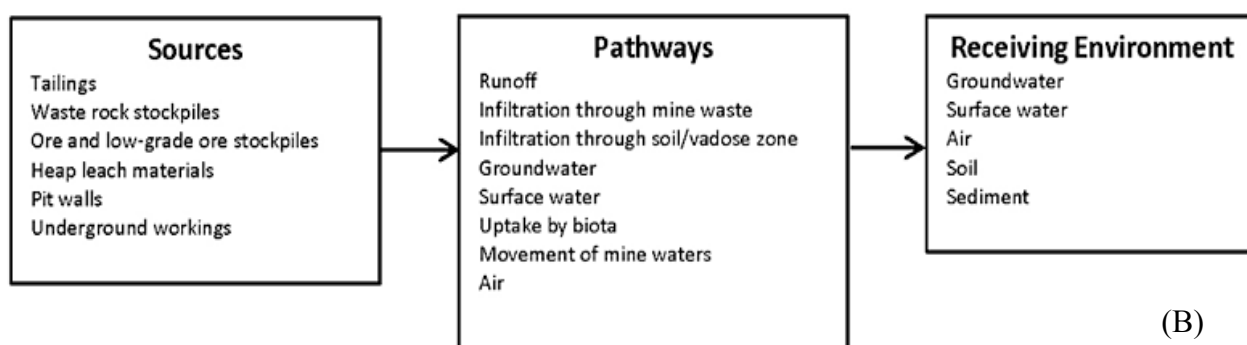


Figure 1: (A) Model of AMD sources, pathways and receiving environments at a mine site (B) Factors affecting sulphide oxidation and AMD composition during transport (Taken from: INAP, 2014 p.93, 106)

Factors that govern the rate of sulphide oxidation

The type of sulphide mineral affects the oxidation process. Not all sulphide minerals generate acidity when oxidised (INAP, 2009). Fe sulphides (pyrrhotite, pyrite, marcasite), sulphides with metal/S molar ratios <1, and sulphosalts generate acid when they react with oxygen and water. Sulphides with metal/S molar ratios = 1 (e.g. chalcopyrite, sphalerite, galena,) tend not to produce acidity when oxygen is the oxidant (INAP 2009). However, when aqueous ferric Fe is the oxidant, all sulphides generate acidity (INAP, 2009). Oxidation rates vary amongst sulphide minerals (Dold, 2010; Lapakko, 2002; Jambor and Blowes, 1994). Reactivity from most reactive to least is:

marcasite → pyrrhotite → sphalerite → galena → pyrite → arsenopyrite → chalcopyrite → magnetite

The quantity of sulphide content will impact the rate and acid forming potential. For example, in the northern Appalachians and Allegheny Plateau, certain coal strata have higher S content (0.8-4wt%) and tend to cause high AMD problems if untreated (Pond et al., 2008). By way of comparison, coal of the western coalfields in NSW, is considered low in S (<1 wt%) averaging at 0.55-0.65 wt% however AMD can still form at these levels (USGS, 2009; NSW PAC, 2012).

Carbonates as a source material can lead to neutralisation of acidic solutions. The neutralisation causes the precipitation of metals present in the mine water drainage (Plumlee et al., 1999). Physical surface area and permeability of the carbonates will also play a significant role in the rate of oxidation (INAP, 2014). There are a variety of sources of carbonates produced through mining including lime used in the neutralisation of AMD that increases buffering capacity (Figure 1A.).

Mine waste, such as tailings, have a high surface area and are highly permeable (Akcil and Koldas, 2006). High permeability leads to high oxygen and water inflow, increasing reaction rates and bacterial activity, leading to increased oxidation (Figure 1). A high surface area increases the available reaction sites thus increasing oxidation (Akcil and Koldas, 2006).

Bacteria plays a significant role in accelerating reactions involved with sulphide oxidation. Bacteria *Acidithiobacillus ferrooxidans* is capable of catalysing both the oxidation of S and ferrous Fe (Akcil and Koldas, 2006). The oxidation rate of ferrous Fe to ferric Fe can be increased by 5 to 6 orders of magnitude by *A. ferrooxidans*, leading to rapid increases in acid production (INAP, 2014).

Factors modifying drainage composition at source

Characteristics of the source site will influence the composition of the resulting drainage. A change in pH in mine drainage usually has the greatest impact on metal(loid) composition. When pH is lowest at the source, metal solubility is at its highest. As drainage moves away from the source material, pH typically increases as a result of dilution from other water sources and the absence of

acid forming sulphides, in turn reducing the quantity of soluble metals (INAP, 2014). Additionally, when mixing of different water types occurs, chemical interaction between water and neutralizing minerals (such as Ca carbonate) may also lead to an increase in pH (INAP, 2014). Together these factors lead to a reduction in potential toxicity as pH increases, as well as metal concentration as metals precipitate.

Climate will determine the volume of flow and whether flow will be continuous or intermittent, leading to a dilution of concentrated solution (unless groundwater is the main water source) (Plumlee et al., 1999; Boyle, 1994). The hydraulic characteristics will determine the residency time between the source material and solution (e.g. rapid preferential flow vs. gradual matrix flow) and the proportion of mine waste being flushed and leached (INAP, 2014). Typically, the higher hydraulic conductivity of the source material, the greater the potential for effective transport of the sulphide oxidation products (Plumlee et al., 1999).

Factors modifying the composition of drainage once discharged from the facility by the receiving environment

The physio-chemical conditions of receiving environments, such as watercourses and groundwater aquifers, also impact on AMD composition. The effect of AMD on the environment is determined by the: flow (dilution), pH and buffering capacity of the receiving stream. Dilution is a function of climate, catchment size and specifically the hydraulic characteristics in groundwater. Dilution will (usually) increase pH as it is mixed with naturally higher pH level waters, reducing the concentration of metals (Nordstrom and Alpers, 1999; Smith, 1999; Plumlee et al., 1999). The hardness of the receiving waters plays a role in neutralization. The higher the bicarbonate and carbonate (hardness) concentration the greater the buffering capacity, raising the pH, precipitating metals (Glass et al., 1982).

Impacts of AMD on receiving waters

A combination of low pH and dissolved metals entering surface water can impact aquatic ecosystems, human health and infrastructure (Gray, 1997). To manage these adverse impacts, government guidelines, such as the Australian and New Zealand Guidelines for Fresh and Marine Water Quality guidelines (ANZECC 2000), provide government regulators, industry, consultants, community groups and catchment and water managers a framework for managing ambient water quality. This is achieved through establishing environmental standards for different chemical and physical water quality parameters for different areas and water uses. These standards then inform if and how conditional approval should be granted for certain activities. If approval is granted the standards are also used by environmental regulators to set pollution standards.

Guidelines are also used to protect aquatic life. These are used to define the chemical, physical, biological and ecological ranges for specific species (Figure 2). If an activity, such as AMD, discharges water outside the tolerable conditions, this will adversely impact the health of aquatic systems (e.g. Herlihy et al. 1990, Maltby and Booth 1991, Winterbourn and McDuffett 1996, Verb and Vis 2000, Cherry et al. 2001, DeNicola and Stapleton 2002, Freund and Petty 2007, Gaikwad et al., 2011; Gray, 1997).

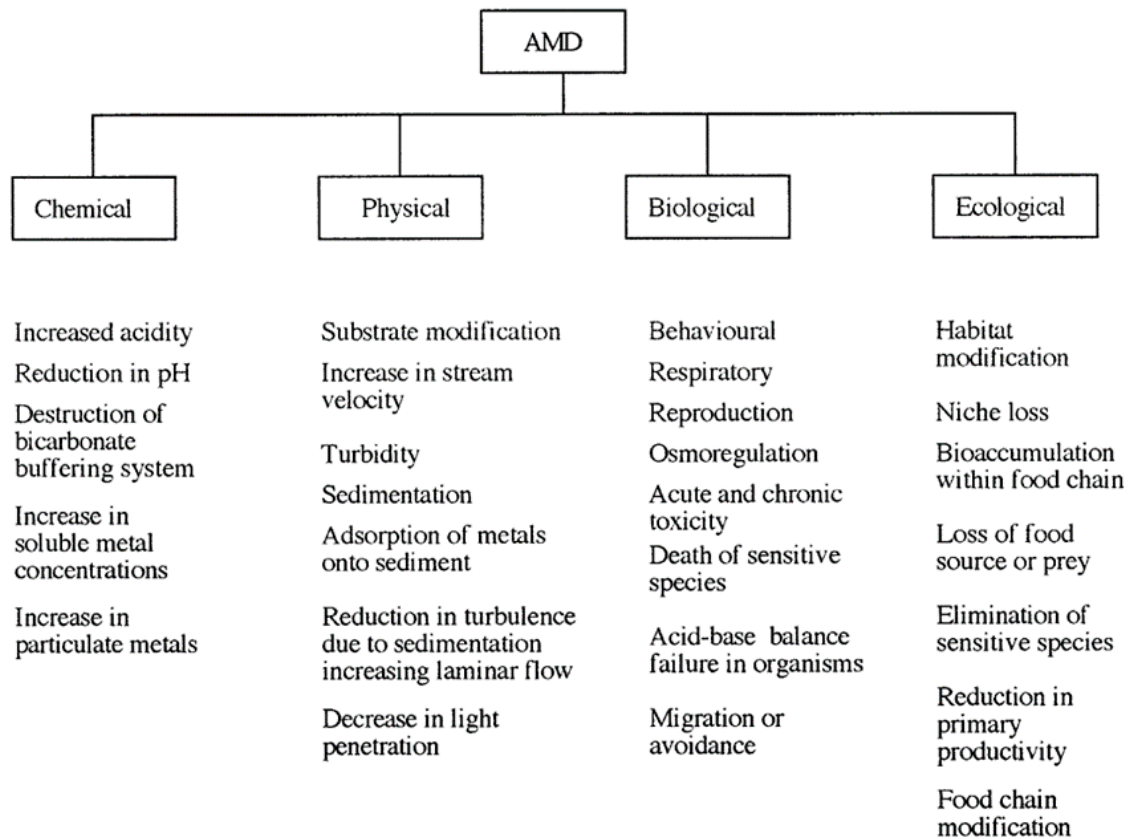


Figure 2: The chemical, physical, biological and ecological impacts on aquatic ecosystems (taken from Gray, 1997 p. 63)

The buffering capacity and dilution of mine waste water will have a significant impact on the effect of AMD (Figure 3). AMD can result in metal toxicity and changes to sedimentation processes. Acidity alone will cause a significant impact on aquatic ecosystems. If pH falls below or above an organism's tolerance range it can result in numerous sub-lethal effects (e.g. diminished growth and reproduction rates) or death due to respiratory (increases in gill permeability) or osmo-regulatory failure (Kimmel, 1983). Typically, macro invertebrates, algae and plankton are most sensitive to pH change (Lenntech, 2014). These organisms form the foundation of the food web, which in turn impact higher order species. As pH becomes more acidic, significant changes in species assemblage occurs leading to the dominance of undesirable algae and macroinvertebrates. At pH of 5 fish species (that are not specifically adapted) begin to reduce in abundance and at pH 4.5 watercourses have been reported to be devoid of fish (Lenntech, 2014).

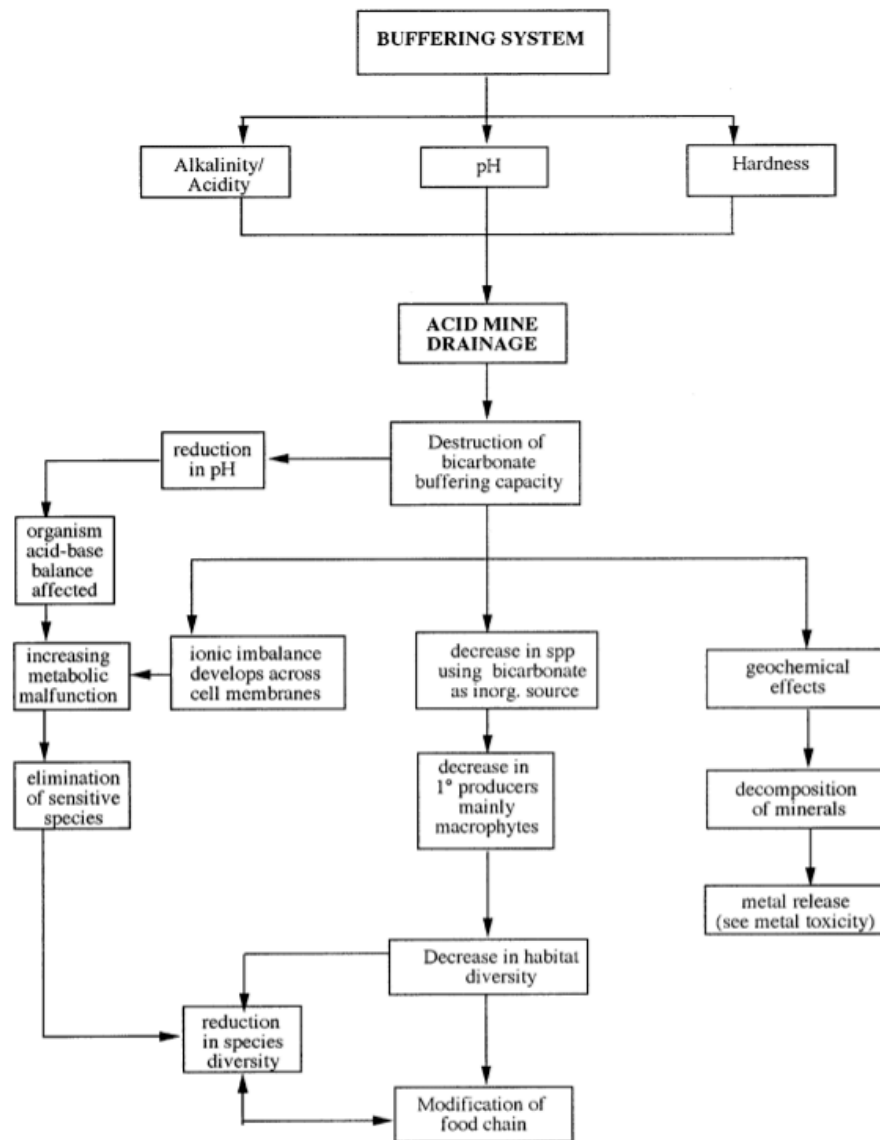


Figure 3: Impact of AMD in relation to pH and buffering capacity (Taken from: Gray, 1997 p. 64)

The pH of water and soils also plays a significant role in metal toxicity and solubility. Metal solubility increases in acidic pH ranges. This not only occurs in metals present in the drainage but in sediment due to dissolution (Figure 4). Aquatic organisms accumulate heavy metals from contaminated water through direct exposure and through bioaccumulation and biomagnification (depending on the metal) in the food chain via indirect pathways (Khayatzaheh and Abbasi, 2010). Metals are persistent in the environment and can be toxic at trace amounts, causing potential oxidative stress in aquatic organisms (Jiwan and Kalamdhad, 2011). For example, Cd, Cu, Ni and Zn are metals of concern because of their severe toxicity to aquatic life at low concentrations (Simate and Ndlovu, 2014).

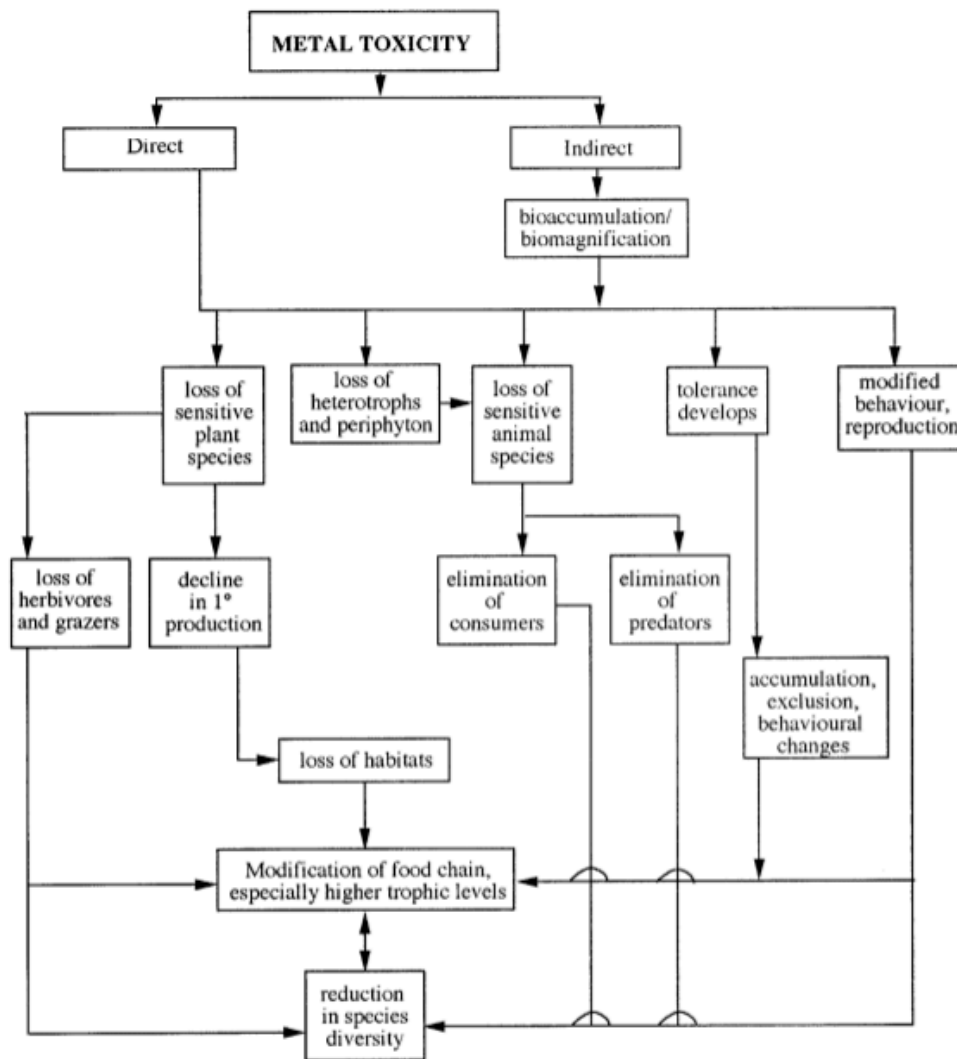


Figure 4: Impact of metal toxicity of aquatic ecosystems (Taken from: Gray, 1997 p. 65)

For some metals, such as Pb, Zn and Ni, concentrations as low as 10 µg/L are known to be toxic to sensitive freshwater species, however ecosystems can function under natural trace amounts of these metals. Acute exposure of these metals can kill aquatic organisms and destroy habitats, while chronic exposure results in mortality or non-lethal effects such as deformities, impaired reproduction success, stunted growth and lesions (Lewis and Clark, 1997). Species assemblages are also impacted, modifying the food web. Increased levels of carbonates (hardness) will reduce the toxicity of Zn and Ni (Cooper et al., 2009; Hyne et al., 2005; Eisler, 1993). Zn impacts enzymes which regulate RNA and DNA, the epithelium of fish, growth, survival, and reproduction of aquatic organisms (Eisler, 1993). Ni toxicity reduces photosynthesis, growth, and nitrogen fixation abilities of algae impacting growth, in turn ecosystem function. Fish are also impacted through the destruction of the gill lamellae causing blood hypoxia. (Eisler, 1998).

The use of Ephemeroptera, Plecoptera and Trichoptera (EPT) richness index is one of the most widely used biotic indices for measuring impairment to stream macroinvertebrate health (Sheehan

1984; Plafkin et al. 1989; Barbour et al. 1992; Hickey and Clements 1998; Camargo et al. 2004; Kitchin 2005; Metzeling et al. 2006). The macroinvertebrates that comprise the EPT index are sensitive to AMD, particularly Ephemeroptera. In Wright and Burgin (2009), reported EPT species richness reduced by 65% and abundance reduced by 90% downstream of the discharge from Canyon Colliery in the Grose Valley, Blue Mountains. This was due to the AMD and associated high levels of Ni and Zn (190 µg/L and 594.7 µg/L respectively).

In addition to dissolved metals and pH, precipitated Fe and Al hydroxides can lead to a reduction in dissolved oxygen. Precipitates also coat surfaces such as gills, eggs, plants and the bed of the stream, directly impacting on a species and reducing habitat for benthic organisms (Hoehn and Sizemore, 1977). Increases in turbidity and sedimentation reduce benthic habitat and growth of benthic organisms and vegetation growth and can cause metal toxicity (Parsons, 1968; Warner, 1971).

AMD Treatment

Lime Neutralisation and precipitation

There are many biological and chemical technologies used to treat AMD. Neutralisation is the most popular method and is typically undertaken using lime, although other alternatives can be used including: caustic soda, slaked lime, quick lime, Mg hydroxide and mineral carbonates (e.g. limestone and fly ash) (Figure 5) (Aube, 2004). The principle of the treatment lies within the insolubility of metals in alkaline conditions. The purpose of a neutralisation treatment is to raise the pH of the raw AMD up to a desired set point where metals become insoluble, causing them to precipitate as hydroxide particles (Figure 5) (Aube, 2004).

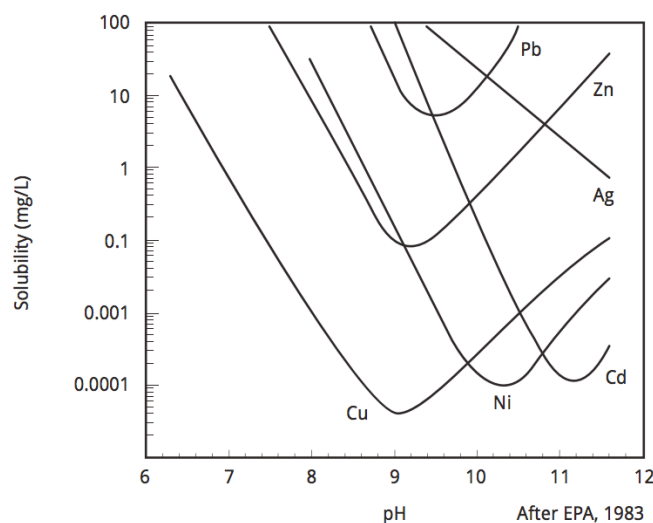
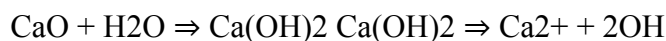


Figure 5: Solubility of metals in relation to pH (Taken from: Aube, 2004 p.2)

In the neutralisation process, lime is slaked and fed into the treatment as a slurry increasing the pH (eq2.).

equation (2)



The pH increase produces hydroxide ions which combine with solute metals to produce precipitates. The particles are then separated to produce a ‘treated’ effluent to meet the desired pollution licence discharge criteria. The separation of liquid effluent and solids forms a sludge containing 1-30% of solids by weight. There are several different forms of lime neutralisation treatment: conventional plants (low density sludge), high density sludge plants (HDS), geco process, staged neutralisation as well as pond, pit treatments and oxic/anoxic limestone drains and channels (Aube, 2004; Johnson and Hallberg, 2005). The main difference being the method of precipitating and separating of the solids and the sludge/solid weight % that is formed. The resulting effluent chemistry is similar however stability of precipitates will change i.e. potential to become resolvable.

Conventional lime treatment plant

The conventional treatment plant directly neutralises AMD in a lime reactor in which pH is controlled by the addition of lime. The resulting slurring is mixed with a flocculant and fed into a clarifier, where the treated effluent is separated from solids, which are collected from the bottom of the clarifier. The treated effluent is typically released directly into the desired discharge site or into a polishing lagoon to reduce residual suspended solids.

Change to neutralisation treatment beyond conventional lime dosing

The HDS is the standard in AMD treatment for coal mines. This process has advantages over conventional lime treatment plants, including: reduced scaling in reactors; improved solid/liquid separation; reduced lime consumption; and increased sludge density. Increasing sludge density is important as it reduces the chance of remobilisation through increasing stability and reduces costs of disposal. Other techniques include Geco and staged neutralisation that can achieve faster settling rates with lower lime consumption. Staged neutralisation steps pH to match different metals points of insolubility leading to more stable and effective metal removal.

Treatment alternatives

It is now understood that tailored treatment solutions are needed as site geology and mining practices influence pH, water quality (suspended solids, conductivity) and variations of metal(oids) present (Balasubramaniam and Panda, 2014). Treatment trains provide opportunities to maximise neutralisation and targeted metal removal. Increasingly the use of membranes nano filtration (NF) and reverse osmosis (RO) is emerging as part of the treatment train where higher levels of treatment

and contaminate removal is required. In terms of water effluent quality, membranes produce the highest level of treatment. RO utilises a smaller pore size and in turn provides complete desalination compared to NF. RO and NF are known to provide similar rejection performance for polluting metals and water softening (Zhong et al., 2007; Carvalho et al., 2011). Both RO and NF technologies are subject to membrane fouling in treating mine waste water (URS, 2014; Schäfer et al., 2004). Membrane fouling is caused by metal oxides, suspended solids and carbonates present in the wastewater that have not been removed from previous treatment steps, variations in pH because of AMD, natural acidity, buffering from limes or hydroxides and the presence of chlorine (that may have been added as part of a pre-treatment) (URS, 2014; Schäfer et al., 2004). Care needs to be taken with RO as the treatment removes virtually all-ionic composition of discharge water, which may be potentially toxic to certain ecosystems. As RO requires circum-neutral pH; before discharge into naturally acidic or alkaline streams, buffering through dosing of acidic or alkaline material as well as the correction ionic composition to match the pH and ionic composition of the natural conditions.

Ion exchange has the capacity to reduce water hardness, desalination, alkalinity removal, and metal removal (URS, 2014). Ion exchange resin can be created specially to cater for treatment needs. For example, strong acid resins (SAR) are best suited for AMD (Khan and Kordek, 2014). Resins have a priority in removing ions. Prioritisation for cations on SAR is: $Pb^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Mg^{2+} > K^{+} > NH_4^{+} > Na^{+} > H^{+}$. (Khan and Kordek, 2014; ITRC, 2016). Hence they are very effective at targeting metals as well as effective water softeners, evident where Ca^{2+} cations are second in the SAR hierarchy, which makes them an effective treatment post lime neutralisation. There are pitfalls with resins. Prioritisation of metals can be an issue in AMD containing a variety of metals and resins need to be regenerated routinely. Pre-treatment is also necessary to ensure resin efficiency and effectiveness. Resins require a pH of 4-8. They are not effective for high quantities of Fe, Mn and Al (particular issue for coal and AMD). Suspended solids can also clog resin beds and strong oxidants and sulphide can degrade and exhaust resins (ITRC, 2016).

Naturally occurring products such as zeolite can also be used in treatment having both adsorption and ion exchange properties (Wingenfelder et al., 2005). For example, clinoptilolite (a zeolite) prioritisation is: Fe^{3+} and $Al^{3+} > Cu^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+}$ (URS, 2014). The high selectivity of Pb, Cd, and Zn is ideal in metalliferous mine water treatment. However, the high selectivity of Fe and Al is an issue especially for AMD and coal mine waste water, which leads to selective exchange of these metals, leading to in-effective treatment of

other metals and high maintenance (URS, 2014). Thus, pre-treatment is necessary in these scenarios where Fe and Al is removed (URS, 2014).

However, treatment trains are not always successful and need to be carefully planned to meet pollution targets and what flux of water needs to treat. For example, at Appin Colliery located in the Sydney Basin, the discharge water at the site is very high in conductivity and dissolved metals. At the site solids are settled out in settling ponds, micro filtration and granular activated carbon removes some metals, organics and TDS, water softeners (ion exchange resins) removes metals as well as carbonates and then reverse osmosis is used as an end treatment to desalinate water and remove any excess dissolved metals and carbonates in solution (BHP, 2015). Even with the use of RO conductivity is still significantly elevated at 1000us/cm. pH of the discharge water is also 8, which does not match the naturally acidic conditions. Even in what would be theoretically close to an ideal treatment for the site, it shows that more research needs to be completed for treatment of the these coal mines in the Sydney Basin.

Metal solubility as a function of pH in aquatic environments

The pH and dissolved oxygen (DO) conditions affect the mobility of heavy metals in aquatic ecosystems (Munk and Faure 2004, Calmano et al. 2005, Cappuyns & Swennen 2005, Temminghoff et al., 1997). Isolating the effect of pH on metal solubility from mines after the licenced mine water discharge point is relatively understudied. In previous studies, low pH values in streams from mine affected discharge generally coincided with high concentrations of dissolved trace metals, as acidic conditions contributed to trace-metal mobilization and transport (Moran and Wentz, 1974; Kimball et al., 1994; Broshears et al., 1996). In contrast, high pH values are associated with areas where rocks/sediment have substantial buffering capacity (alkalinity) commonly coinciding with low concentrations of trace metals. However, metals such as Mn and Zn can have high solubility in neutral water (Stumm and Morgan, 1981).

Sediments play an important role in how metals impact on aquatic ecosystems. Sediments can act as both a source and sink for metals. Approximately 90% of metal load in aquatic systems is bound to sediment and particulate matter (Zheng et al., 2008; Amin et al., 2009; Calmano, et al., 1993). This is due to the ongoing process of reduction and oxidation that removes dissolved metals from the water column and binds them to sediment particles (Cohen, 2002). Metals in the form of suspended particles also settle out into the sediment. Sediments reflect the long-term metal composition of a watercourse, while water exhibits significant temporal variation in metal levels. Sediment composition can also play a significant role in metal solubility. Sediments are complex and a result of interacting geologic, geochemical, biological, and climatic processes. This is further complicated

by AMD, which causes high quantities of soluble metals and secondary precipitates as well as secondary minerals such as yellow- to orange hydrous ferric oxides and Fe hydroxysulfates, and white Al hydroxysulfates. Buffering capacity will impact metal solubility and help determine the pH of the receiving water. This is particularly relevant in areas of underlying geology that are high in Ca (high buffering capacity) or with high silicates (low buffering capacity) (Plumlee et al., 1999).

The impact of pH on the solubility of metals in reservoirs, estuaries and ocean sediments has been relatively well studied, typically involving locations with high buffering capacity and sulphides, impacting solubility characteristics of different metals (Szarek–Gwiazda, 2014; Tack et al., 1996; Trefry and Metz, 1984). In Australia, at least, sediments are often overlooked in environmental regulation and pollution licencing (Cohen, 2002). Determining the relationship between pH and metal solubility from sediments is essential if the aim is to minimise the impacts of coal mining on aquatic systems.

The solubility of metals varies due to the buffering capacity; however, patterns emerge between the solubility of different metals. Szarek–Gwiazda (2014) analysed the release of metals from sediments in Carpathian reservoirs at different pH. She found that a decrease to pH 5 resulted in significant release of Cd (35%), Pb (39%) and Mn (60%) and a lower release of Zn (14%), Cu (18%) and Fe (1.5%). Cd, Mn and Zn solubility was linear with decreasing pH from pH 7, while Cu, Fe and Pb levels saw rapid increase below pH 3. The study showed that the lowering of pH yielded potential to remobilise metals, however several factors influenced the results. Sediments in the reservoirs had a high buffering capacity. Elevated levels of in Cd, Pb and Mn were due to these elements being present in larger amounts as exchangeable and carbonate forms in the sediments. This meant that acidification of the sediment led to the dissolution of carbonates resulting in the release of the associated metal ions (Buykx et al. 2000). However, general shapes of solubility characteristics were found with differences between the sites due to different buffering capacities.

Trefry and Metz (1984) reported similar results analysing sediments from the Mississippi Delta and Gulf of Mexico. They found Cu, Fe and Pb levels followed similar patterns with a sharp increase in concentrations below pH 4-3, while Cd and Mn showed linear increases from pH 7. Zn removal followed the same pattern in Szarek–Gwiazda (2014), a gradual linear increase with decreasing pH (like Mn) but with a small percentage of total metal leached at each pH. Tack et al (1996) analysed the solubility of sediments in relation to pH under different oxidising conditions in dredged ocean canal sediments. Solubility of Cu, Pb and Zn in flooded and aerated sediments and flooded reduced sediments was low due to the presence of sulphides. Metal sulphides are highly insoluble even in strong acid conditions. The metals Co, Ni and Mn were often associated with carbonates, with solubility increasing linearly as pH reduced in a similar way to those in Szarek–Gwiazda (2014) and

Trefry and Metz (1984). However, for Cd and Zn, solubility increased somewhat linearly in aerated and mixed sediment, however did spike at pH 2.

Measuring metal solubility at different pH

There is no standard for analysing the impact of pH on metal solubility, however several methods have been used in leaching procedures such as the toxicity characteristic leaching procedure (TCLP) and pHstat (Cappuyens et al., 2004a, 2004b, 2005; Van Herreweghe et al., 2002; Tackett et al., 1986). TCLP has been widely used due to its ease of completion and replication and produces accurate results. However, pHstat tests allow for the analysis of in situ solubility changes.

Moreover, information can be obtained on the potential buffering capacity of the sample and its sensitivity to pH changes due to external stresses (e.g. soil acidification, liming). This is achieved using a pH electrode and an automatic potentiometric titration using an automatic titration dispenser. Samples of the suspension can then be taken at regular time intervals e.g. 0, 0.5, 1, 3, 6, 12, 24, 48, 72 and 96 h.

In terms of duration needed for the two leaching methods to yield reliable results, Trefry and Metz (1984) showed at pH 2.2, 4, 5, and 6, equilibrium was generally achieved in 12-24 h. In the first 0.5 h of the 48-h experiment, 35% of the leachable Fe and 70-85% of the other metals were removed at all pH levels. This rapid initial release slowed considerably after 12 h. Typically, nitric acid is used in leaching procedures as it serves to prevent the adsorption of metal ions and their precipitation, is antibacterial and keeps a certain degree of oxidizing power, preventing reduction.

Clarence Colliery Case Study

Site Description

Clarence Colliery is located near Lithgow in the Blue Mountains, NSW, Australia. The mine is located near the headwaters of the Wollangambe River (Figure 6). The headwaters of the Wollangambe River are located on the Newnes Plateau, 1.5km NW of Clarence Colliery at 1150m above sea level in the Blue Mountains, NSW. The river stretches 57km flowing E to Mount Irvine then NNE, joining with the Colo River, 55m above sea level (NSW OEH, 2015). The Wollangambe River primarily flows through the Blue Mountains National Park and it also located within the GBMWhA. The upper most reaches and tributaries of the Wollangambe River are located outside the National Park areas within Newnes State Forest, on Crown Land and under private land holdings (Figure 6).

Clarence Colliery is an underground coal mine located on the Newnes Plateau at Newnes Junction, 8.5km east of Lithgow (pit top 33°27'49.75"S, 150°14'47.91"E) (Wright et al., 2017). Mining commenced in 1979 and is still currently operating under three separate development consents.

Underground mining is undertaken within consolidated coal lease (CCL) 705 and Mining lease (ML) 1353, 1354 and 1583 (Figure 7). Mining is located primarily beneath Newnes State Forest to the N and private land holdings and crown land to the S, bordering the Blue Mountains National Park to the E (Figure 6). The surface workings are located on free hold land (Wright et al., 2017).

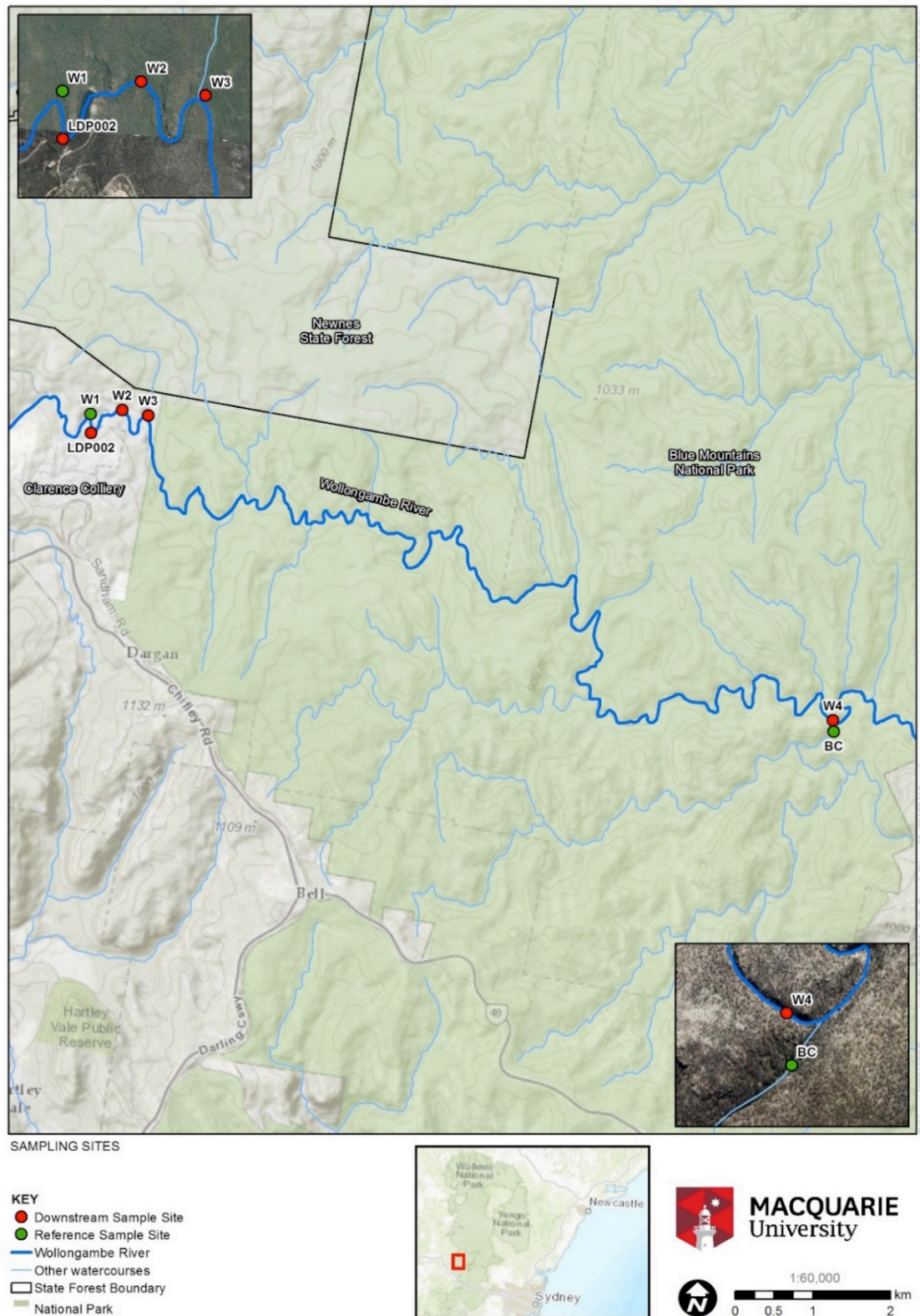


Figure 6: Map showing the study area. Clarence Colliery is shown. The Wollangambe River, Bell Creek and other watercourses can be seen. Reference sites are labelled with green markers, while sites downstream of the discharge are labelled with red markers. The boundary between Newnes State Forest and Blue Mountains National Park is labelled

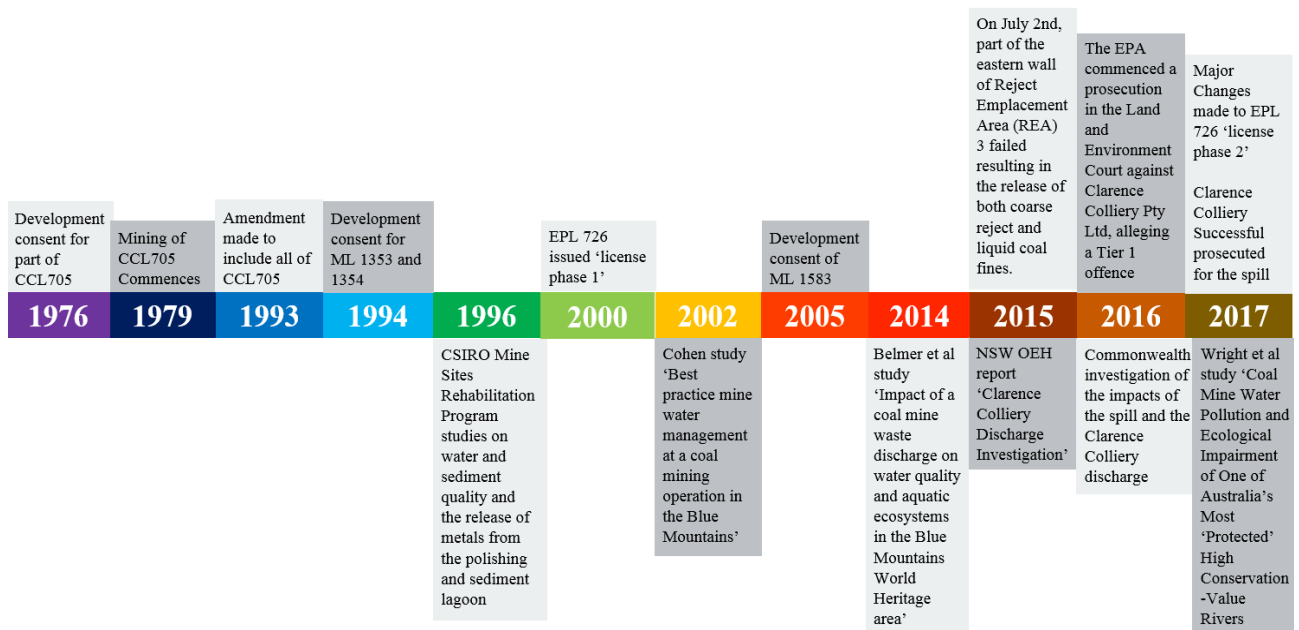


Figure 7: Timeline of events at Clarence Colliery from its development consent in 1976 to the present (2017).

At the site, wastewater is generated from ground water, coal washing processes and run off from pit top activities (Cohen, 2002). Approximately 14ML of groundwater infiltrates underground workings daily (Cohen, 2002). The extraction of coal requires the removal of water through a dewatering process at the surface. Inflow of water occurs through fractures and fissures in the rock and fractures in the roof of the underground workings, particularly in areas subject to pillar extraction during secondary workings. This water produces the AMD (Cohen, 2002). Although the S content of the coal in the seams being mined are very low (0.38wt%) a substantial volume of AMD is produced. The raw mine water has a pH 4.2 containing 0.39 mg/L of Co, 2.04 mg/L Fe, 2.36 mg/L Mn, 0.89 mg/L Ni and 2.6 mg/L Zn (Cohen, 2002).

The discharge of mine water is subject to EPL 726. The terms of the licence are summarised in Table 1. The EPL specifies 100th percentile (maximum) concentration limits for a range of constituents, including: volume (25ML per day) and physical or chemical attributes specified as 100th percentile (maximum) concentration limits: Chlorine, sulphate, fluoride, oil and grease, pH, total suspended solids and metal(oids) Fe, Mn, As, Bo, Cd, Cu, Pb, Hg, Se, Ag, Cr, (Table 1) (EPA, 2017; Graham and Wright, 2012; Wright et al., 2017; NSW OEH, 2015). There have been 2 major phases to EPL 726. Phase 1 prior to the major changes made to EPL 726 on June 5th 2017 and phase 2 post June 5th 2017 (Table 1).

Table 1: EPL 726 including licence prior to major changes ‘phase 1’ and New licence as of June 5th 2017 ‘phase 2’ compared to ANZECC 2000 Guidelines

Chemical/Parameter	EPL 726 Phase ‘1’ Pre June 5 th 2017	EPL 726 ‘Phase 2’ post June 5 th 2017	ANZECC 2000 Guidelines
As (µg/L)	10	13	13
Bo (µg/L)	100	100	370
Cd (µg/L)	1	0.2	0.2
Cl (µg/L)	25000	25000	No limit
Cr (µg/L)	10	1	1
Co (µg/L)	No limit	2.5	No limit
Fe Filterable (µg/L)	300	300	No limit
Fluoride (µg/L)	No limit	1000	No limit
Pb (µg/L)	5	3.4	3.4
Li (µg/L)	No limit	100	No limit
Mn Filterable (µg/L)	500	500	1900
Hg (µg/L)	1	0.06	0.06
Ni (µg/L)	No limit	11	11
Nitrogen (µg/L)	No limit	250	250
Oil and grease mg/L	10	10	No limit
pH	6-8.5	6-8.5	6.5-8.0
Phosphorous (µg/L)	No limit	20	20
Se (total) (µg/L)	10	5	5
Ag (µg/L)	1	0.05	0.05
Sulphate mg/L	250	250	No limit
Zn (µg/L)	1500	8	8

To achieve the water quality requirements in the EPL, mine waste water is treated using a conventional lime treatment plant (Figure 8). The process is as follows: (1) neutralisation of incoming water with lime and potassium permanganate to pH 9.2; (2) water is mixed with alum and a polymeric flocculant to form a sludge; (3) clarifier where sludge is removed (Figure 8). The water is then pumped into the sedimentation pond and then the polishing lagoon. (Cohen, 2002). This water is continuously discharged at site LDP002 under EPA licence (EPL726) (Figure 8). LDP002 flows 200m downstream into an unnamed tributary before entering the Wollangambe River. A further 200m downstream is the Wollangambe Dam, approximately 1.5km upstream of where the river enters the Blue Mountains National Park (Figure 6) (Wright et al., 2017). Reported in September of 2017 the mine discharges an average of 12.3 ML/day (EPA, 2017). The pH of the discharge water ranges from 6.9-8. This compares to the pH of the reference streams of 4.6-6 (Wright et al., 2017; NSW OEH, 2016; Belmer et al., 2014).

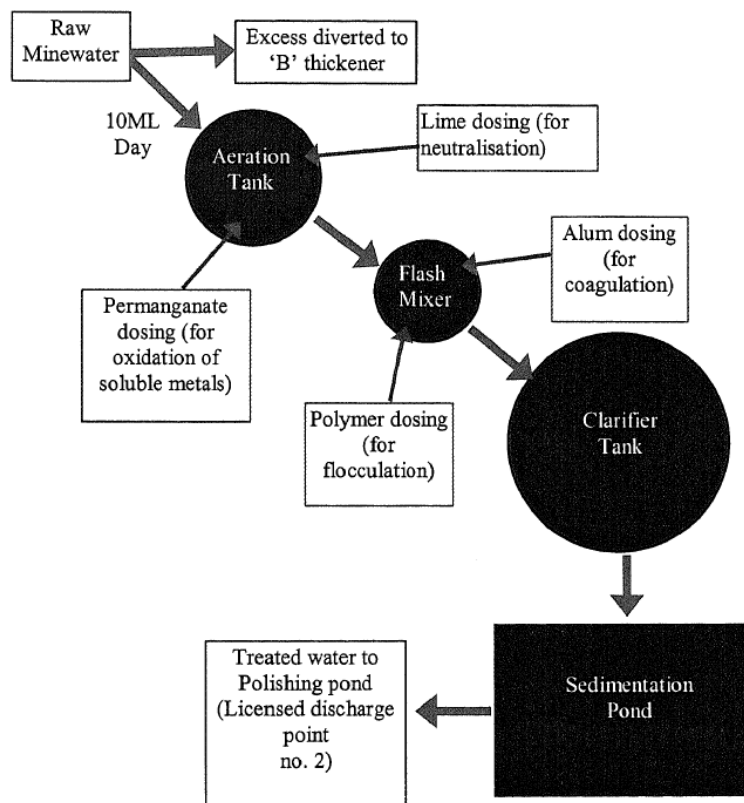


Figure 8: Water treatment plant used at Clarence Colliery (Taken from: Cohen, 2002 p. 103)

Background conditions of the Wollangambe River are characterised as having very low levels of cations and anions. This is due to geology of the region, which is composed of highly-weathered Narrabeen Group sandstone that is primarily composed of quartz. This sandstone group was deposited under non-marine conditions resulting in a small fraction of fines. The resulting sediment in the catchment is primarily all medium to fine quartz sand, resulting in low buffering capacity (Toyer and Main, 1981).

Prior studies

The impact of Clarence Colliery on the Wollangambe River has been the subject of numerous studies (Wright, 2017; Belmer et al., 2014; NSW OEH, 2015; Cohen, 2002). The first study completed on the impacts of coal mining on the Wollangambe River was undertaken in 1996 by the CSIRO as part of a mine site rehabilitation research program (CMSRRP). This was in response to the observation of a black sludge or biofilm on the bed of the Wollangambe River for about 1.5 kilometres downstream of Clarence Colliery. The biofilm was found to be natural and derived its black colour and growth from accumulating Mn oxides, and the entrapment of microfine coal (NSW OEH, 2015). The EPA commenced addressing the high Mn concentration in the mine water, which was well above the Protected Waters (Class P) limit of Schedule 2 of the Clean Waters Regulations 1972, subsequently repealed and replaced with the POEO act (1997). At the time, the

filterable Mn in the mine water ranged from 1.35 to 2.24 mg/L, well above the then Schedule 2 limit for filterable Mn of 0.05 mg/L.

As part of the CMSRRP study, Jones and Riley (1996) analysed the release of metals from the sediment pond and polishing lagoon. It was found there was a 2 to 3-fold increase in dissolved concentration of Mn and Zn between the sediment pond and discharge from the polishing lagoon, confirming remobilisation of some metals. Sediment in the sediment dam contained 4.9 % Al, 4% Zn, 1.2% Ni, 5.5% Mn and 0.58% Co, while the polishing lagoon sediments contained 1.3% Al, 1% Zn, 0.3% Ni, 0.15 % Mn and 0.1% Co on a dry wt basis. The toxicity characteristic leaching procedure (TCLP) was used to determine the optimum target pH for insolubility and to determine the pH at which different metals became soluble. It was shown that a pH in excess of 8.5 was required to maintain Mn levels below 0.05mg/L (Figure 9).

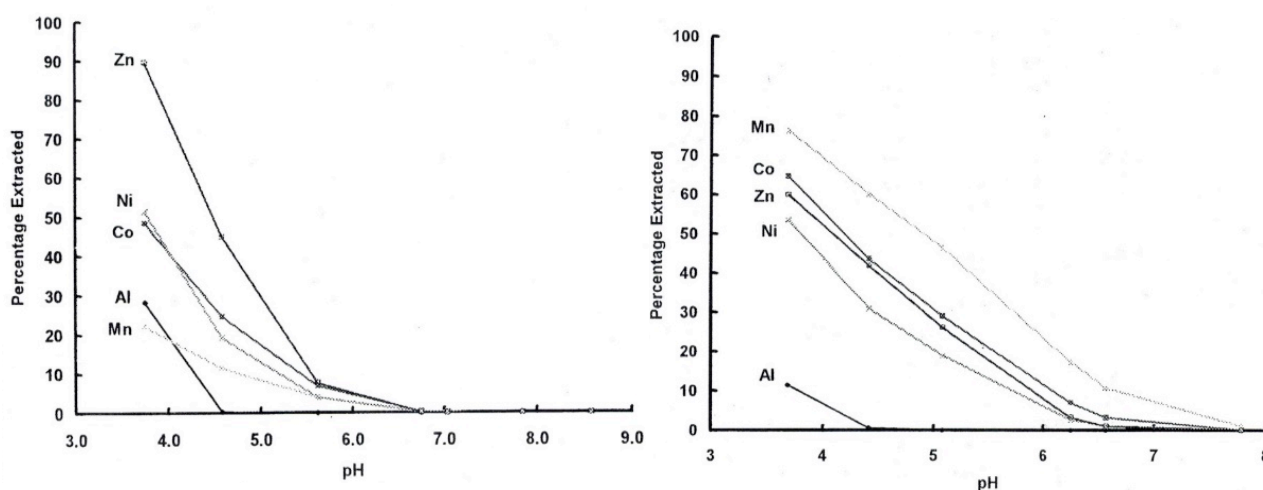


Figure 9: (Left) percentage of total extractable metals at varying pH in the sediment pond at Clarence Colliery (Right) percentage of total extractable metals at varying pH in the polishing pond at Clarence Colliery (Taken from: Jones and Riley, 1996 p. 21, 38).

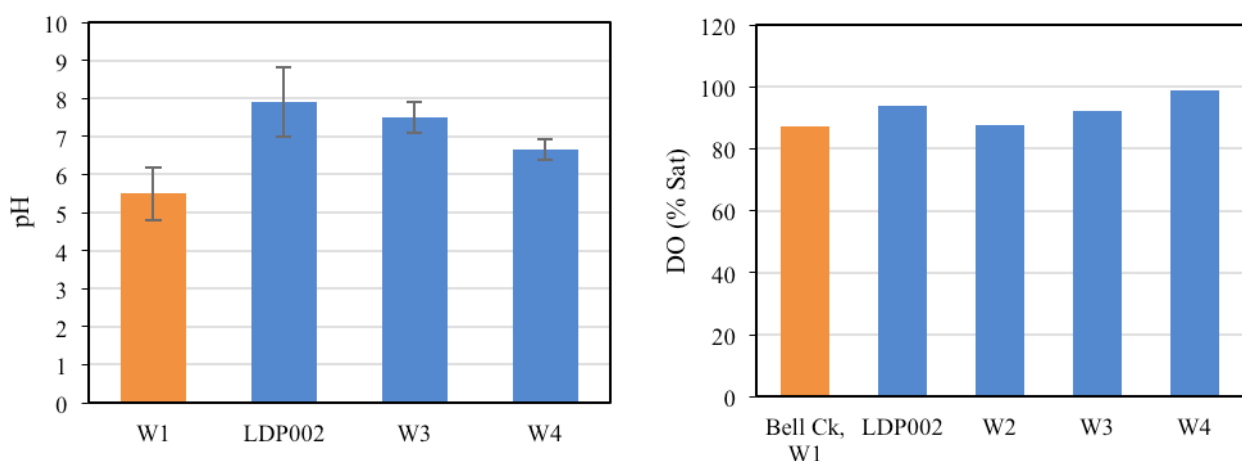
The TCLP indicated Mn was significantly soluble at 7.5 and Co, Ni and Zn at pH 6.6 in the polishing lagoon (Figure 9). At pH 6.6 in the surface sediments (0-30cm) of the polishing lagoon: 0 µg/L Al, 550 µg/L Co, 2420 µg/L Mn, 500 Ni µg/L, 2300 µg/L Zn equating to roughly 13% of total Mn 4% of total Co, 1% total Zn, 0.5% total Ni was extracted from the sediments (Figure 9). It was recommended by Jones and Riley (1996) that the pH of the lagoon be maintained above 7.5 and possibly up to 8.5; to use less permanganate in the treatment and to reduce the amount of additional Mn in the system; and investigate the use of a polyamide based flocculant to replace the use of potassium permanganate.

The second study completed as part of the CMSRRP study was completed by Jones and Eames (1996). Their study examined the quality of water and sediment in the Wollangambe River. They

identified that Al, Co, Fe, Mn, Ni, Zn and S in the Wollangambe River sediment and water downstream of the discharge point were significantly elevated over background conditions above the discharge (Figure 10). Data suggested that precipitated Zn and Mn were being remobilised in the sedimentation pond and polishing lagoon due the pH being too low (i.e. pH 7).

In 2002, Cohen (2002) completed his Honors thesis commissioned by Clarence Colliery on the 'Best practice mine water management at a coal mining operation in the Blue Mountains'. The thesis provided Clarence with best advice on managing AMD, the mine discharge and associated impacts. The study recommended that fissures and fractures should be selectively grouted and the discharge be diverted to Farmers Creek in another catchment outside the national park. It was identified that the treatment plant was ineffective at treating the AMD. This study focused primarily on Mn, noting that the retention time of the plant was not sufficient to precipitate Mn, leading to soluble Mn being discharged. It was reported that precipitated Mn was escaping into the polishing lagoon, where it became soluble in the lagoon and the Wollangambe River due to the pH being too low. The identification of Mn in the downstream waterways also pointed to the limitations of potassium permanganate as a flocculent that, while beneficial for water quality treatment, was concurrently adding to the metal load to the downstream waterways.

Downstream of the discharge to the river Cohen reported that the composition of sediments changed (Figure 10). While the bulk of sediment material was quartz sand there was an increase in fine grained material. He also noted biofilm covered a substantial amount of the river bed. Cohen (2002) reported Ni, Mn, Zn and Co in the sediments were significantly increased at least 20km downstream of the discharge point over background conditions (Figure 10). Ni and Zn concentrations were highest directly below the discharge, while Co and Mn were highest 3km downstream, which is inside the GBMWhA (Figure 10). Mn was strongly associated with the biofilm. Fe and Co were also associated with the biofilm as well as fine grained material and fine sand for Co. Ni and Zn were associated with fine and medium grain sands.



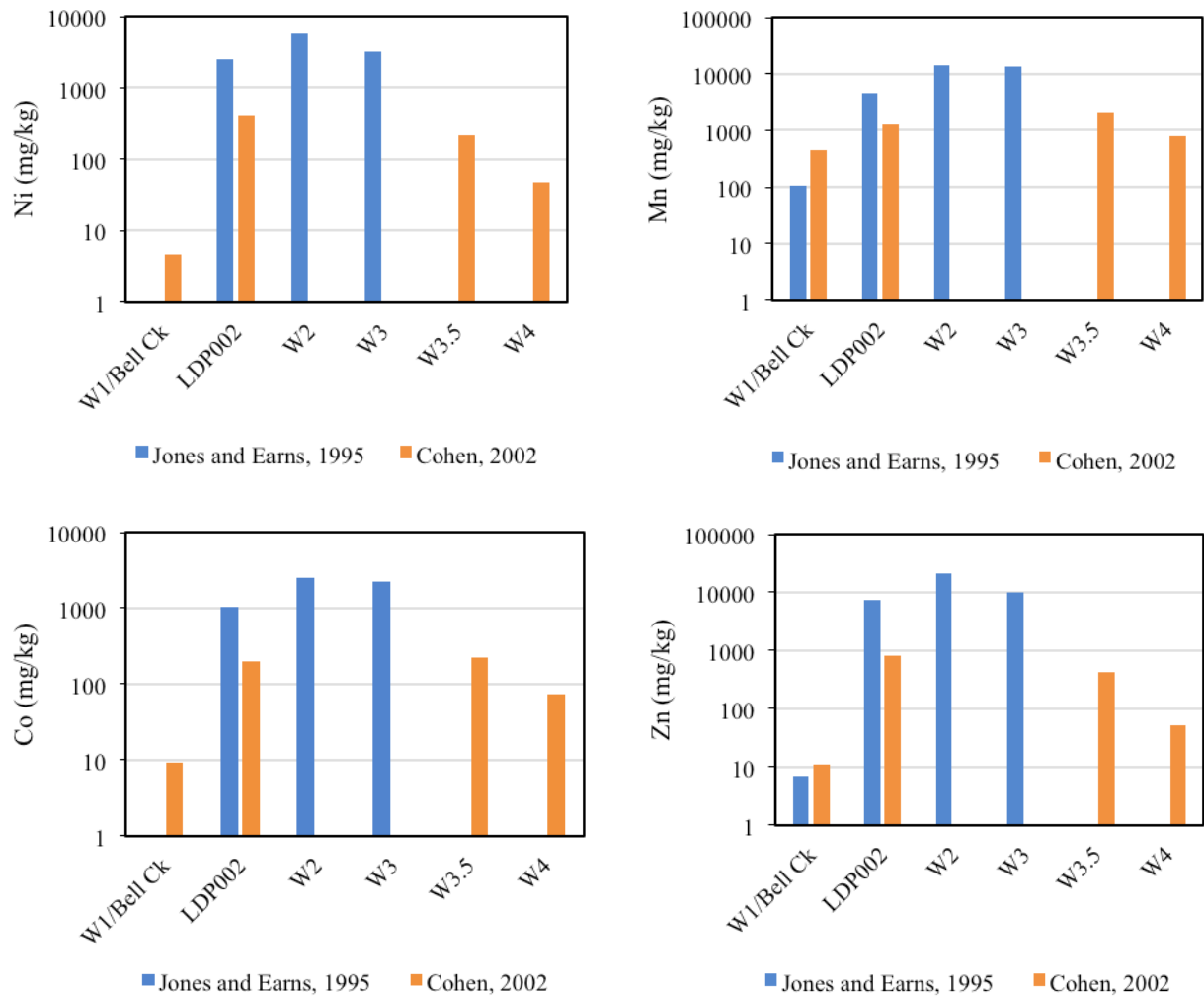


Figure 10: (Top Left) Mean pH readings from Belmer et al., 2014 and Wright et al., 2017 (Top Right) Mean dissolved oxygen reading from Wright et al., 2017 (middle left) Co levels in sediment from Cohen (2002) and Johns and Earns (1996) (Middle Right) Zn levels in sediment from Cohen (2002) and Johns and Earns (1996) (Lower Left) Ni levels in sediment from Cohen (2002) and Johns and Earns (1996) (Lower Right) Mn levels in sediment from Cohen (2002) and Johns and Earns (1996)

The Cohen study (2002) reported similar results to Jones and Eames (1996) (Figure 10). Jones and Eames (1996) indicated secondary remobilisation of metals after the licenced wastewater discharge point. Levels of Al, Mn, Ni, Co and Zn were significantly higher 30m and 150m below the Wollangambe Dam compared to upstream at the discharge (Figure 10). Approximately 2km downstream of the dam, Zn and Ni levels were higher than that of Cohen (2002) but showed the same trend in reducing downstream (Figure 10). Cohen (2002) similarly reported Mn and Co were significantly elevated downstream of the discharge. However, data from Cohen (2002) failed to show the scale of remobilisation influenced by the dam like Jones and Eames (1996) (Figure 10). This was due to the first site analysed being 3km downstream of the discharge.

Between the issue of EPL 726 issued on 1st January 2000 and 2014 only small changes were made to the licence by the NSW EPA. This was in spite of Clarence Colliery being issued two penalty notices from the NSW EPA for exceeding Mn limits. Additional research interest in the site arose from an independent study commissioned by Western Sydney University. The paper by Belmer et al (2014) concluded the mine wastewater discharge significantly impacted aquatic macroinvertebrate communities. Below the discharge there was a decrease in family richness by 65% and abundance by 90%. These changes correlated with a decline in water quality. When compared to upstream reference sites, the river water quality below the mine discharge reported: conductivity 11 times higher; temperature 2.5°C higher; and Zn levels were 101.5 µg/L compared to ANZECC guidelines of 8 µg/L and was 200 times greater than ANZECC guidelines; and pH was 7.2 compared to 5.6. The Belmer et al (2014) report led the EPA to request the NSW Office of Environment and Heritage to assess the impacts of the discharge at Clarence Colliery as part of a statutory review of EPL726 (NSW OEH, 2015). In response to the EPA's request the NSW OEH completed an investigation entitled '*Clarence Colliery Discharge Investigation*' in June 2015 and concluded (NSW OEH, 2015):

- LDP002 introduced a high-volume source of pollution into the Wollangambe River in which little dilution of contaminants is achieved.
- LDP002 introduced elevated levels of: Co, Ba, Li, Mg, Ni, K, Sr, S, Zn as well as sulphate, Ca, TDS, conductivity, hardness and bicarbonate. Ni, S, sulphate and Ca were 50-100* greater than background.
- Zn and Ni were above ANZECC guidelines.
- Ecotoxicology: LDP002 discharge caused acute toxicity of freshwater cladoceran *Ceriodaphnia dubia* at different dilutions. LDP002 also inhibited growth in freshwater green algae *Pseudokirchneriella subcapitata*.
- The LDP002 discharge has the potential to cause toxic and reproductive effects on macroinvertebrate and algae communities in the GBMWA
- The investigation concluded that the review of EPL limits should be based on ANZECC guidelines.

Before action on the OEH report was undertaken, the eastern wall of Reject Emplacement Area (REA) 3 failed on 2 July 2015. This resulted in the release of both coarse reject and liquid coal fines from the site into the Wollangambe River. The EPA issued a clean-up notice the day after the spill, outlining the clean-up requirements that Centennial Coal needed to put in place. The EPA issued a second clean-up notice to the company on the 18th August 2015, which outlined the development of a Wollangambe River Environmental Monitoring Program (WREMP) by the licensee, which was

received in compliance with the licensee on the 25th of September 2015. As of May 2nd, Clarence Colliery reported 208 tonnes of coal fines had been removed at a cost of \$2 million. The EPA commenced legal action in the NSW Land and Environment Court against Clarence Colliery Pty Ltd for this incident under the *Protection of Environment Operations Act 1997*. This resulted in a \$1.05 million fine and costs (approximately \$500,000)

Due to the nature of the pollution spill and its potential impacts on the GBWHA the federal government commissioned a separate study although this has not been publicly released.

Wright et al (2017) published another study reporting that the mine waste discharge had significantly increased pH and conductivity, altered ionic composition, increased the quantity of cations and anions and increased the quantity of Ni and Zn in the river up to 22km downstream. These changes were attributed to a significant ecological impairment as measured by EPT abundance and richness up to and beyond 22km from the discharge point.

In June 2017, the NSW EPA changed the pollution licence for the mine (Refer to Table 1 Phase 2 licence). This was the most significant variation to the licence since the commencement of the mine and represented the cumulative weight of evidence that the mining operation was polluting the environment. However in September of 2017, according to the new EPL726 the mine reported exceedences of Co, Ni and Zn.

Literature Synthesis and Research Problem

Previous research involving the solubility of metals in acidic conditions has focused on lakes, reservoirs and estuarine and ocean sediments i.e. reducing environments (Szarek–Gwiazda, 2014; Tack et al., 1996; Trefry and Metz, 1984). Clarence Colliery presents an example unlike others researched: the river is near pristine pre-discharge, showing a clear and direct impact from discharge; it is in the headwaters of the catchment; freshwater; oxidising; has low buffering capacity; and is naturally acidic.

Past research on the Clarence Colliery on the Wollangambe River have clearly described and quantified the impact of the mine on the environment. This has included water and sediment quality and the cumulative impacts on the ecology within the river. However, a gap in the research to-date, has been to examine the role of contaminated sediments that have been discharged (under licence), to the river as a potential ‘reservoir’ of metal sand other pollutants. The criticality of these contaminated sediments lies in the solubility of metals under naturally acidic conditions and their contribution to the ongoing contamination of the Wollangambe River.

The importance of this issue is pertinent to the current operation and regulation of the mine and its eventual closure. Jones and Riley (1996) foreshadowed the potential of remobilisation of metals in the sediment lagoon through TCLP analysis, although they did not identify this as a concern for sediments discharged into the river. What is not known are the quantity of sediments already in the river as a result of previous mining operations, nor their long-term contamination potential. This is in spite of 20 years of research that has identified metals in sediment as an issue, but which remain unregulated. Furthermore, it is well understood that as pH reduces to background conditions (acidic) coupled with the lack of natural buffering capacity this is likely to increase solubility of the metals bound in the sediment, which in turn will add to the pollutant load already impacting the Wollangambe River.

Methods

Study Design and Sample Sites

Longitudinal Study

The study was conducted in the upper to mid Wollangambe River catchment (Figure 6). A longitudinal method was used to determine the impact of the mine discharge on pH, ionic composition and metal quantities downstream. The methods relied on an analysis of water and sediment to assess the impact of the mine on the downstream environment. In total, six sites were chosen using an ‘after, control versus impact’ (ACI) design (Table 2, Figure 6) (Underwood, 1991).

Table 2: Study sample locations and description

Site name	Site Code	Co-ordinates	Altitude (m)
Wollangambe River 200m above LDP002 (REF)	W1	33°27'20.36"S 150°14'58.33"E	996
200m below licence discharge point	LDP002	33°27'28.55"S 150°14'58.72"E	993
Wollangambe River 1.2 km downstream of mine discharge	W2	33°27'18.35"S 150°15'14.00"E	971
Wollangambe River 2km downstream of mine discharge	W3	33°27'20.41"S 150°15'26.90"E	955
Wollangambe River 21km downstream of mine discharge	W4	33°29'20.81"S 150°21'12.67"E	755
Bell Ck (REF)	BC	33°29'25.42"S 150°21'13.39"E	756

Typically a ‘before, after, control versus impact’ design is ideal, however as no data was collected at site prior to the mine discharge, no before could be obtained. For the control, 2 pristine reference sites were used for comparison with four sites were taken downstream of the discharge as the after to determine the impact. The sites selected have been used in prior studies (Jones and Eames, 1996; Cohen, 2002; Belmer et al., 2014; NSW OEH, 2015; Wright et al., 2017) and helps improve the data set for comparison of water and sediment composition over time. Multiple reference sites were used; W1 upstream of the mine and Bell Ck (BC), upstream of the confluence of BC and the Wollangambe River at Mt Wilson (Figure 6, Figure 11). These two sites provide an example of how the sites downstream of the mine should be without the discharge, both chemically and physically. Three sites were chosen closely downstream of the discharge point at 200m, 1.2km and 2km (LDP002, W2, W3 respectively) to determine the immediate impacts of the discharge on water and sediment composition (Figure 6, Figure 11). Also, the impact of the dam between LDP002 and W2 can be assessed (Figure 11).





Figure 11: Images of field sites. Each site is labelled.

These downstream sites were all located upstream of the Blue Mountains National Park boundary (Table 2) (Figure 6). The W4 site was located 21km downstream of the discharge point within the Blue Mountains National Park near Mount Wilson (Figure 6) to determine the spatial impact of the mine waste water on the river. To investigate the full impact of the mine, more sites could have been analysed, i.e. between W3 and W4 and in the Wollangambe Dam. However, this was largely constrained by accessibility given the rugged terrain and canyons between sites W3 and W4.

Water and sediment chemistry was investigated three times for each site, providing three sample replicates at different times (dates sampled 10/2/17, 21/3/17, 15/4/17). At each site, physiochemical water properties: pH, Dissolved oxygen (DO), temperature and electrical conductivity (EC) were measured using a TPS AQUA meter. Water samples were collected using clean unused sample bottles provided by a commercial testing laboratory. Separate sample bottles were used for cations and anions (no nitric), total metals (nitric preservation) and dissolved metals (nitric preservation)

which were passed through a 0.45 µm filter using a syringe. Samples were chilled after collection for delivery to the laboratory on the same day. All water samples were analysed using standard methods (APHA 1998) by a National Associations of Testing Authorities (NATA) accredited laboratory, measuring: ionic balance (Ca, K, Mg, Na, Hardness, hydroxide, carbonate, bicarbonate, total alkalinity, chlorine and sulphate) and total and dissolved metal(oids) (As, Cu, Al, Fe, Mn, Ni, Co, Zn, S, Ba, Sr and Pb) using ICP-MS. Analytical QA/QC procedures included the use of de-ionised water blanks and spiked samples. Results from the water analysis were compared to EPL726, ANZECC (2000) guidelines and prior studies (e.g. Cohen, 2002; Belmer et al., 2014; NSW OEH, 2015; Wright et al., 2017).

Sediment was also collected following AS/NZS standards (AS/NZS, 1999). Sediment at the site was primarily coarse to medium sand with minor fine-grained material. Approximately 100g of sediment was collected in glass sample containers for ICP-AES analysis to determine the quantity of different metals in the sediment at high resolution, including: As, Cu, Al, Fe, Mn, Ni, Co, Zn, S, Ba, Sr and Pb as well as Ca and S. Depth and the amount of sediment available was often minimal due to the bedrock confined nature of the river and being in the upper reaches of the catchment. Thus, effort was taken to sample from areas with a sediment depth of at least 20cm, in which the top 5cm was not sampled to ensure none of the biofilm was included in the sediment sample and to maintain consistency among samples. Samples were then stored in an ice box at 4°C for transport. Samples for ICP-AES analysis were taken the same day to a National Associations of Testing Authorities (NATA) accredited laboratory for analysis. QA/QC included the use of Australian Government Analytical Laboratories reference material 10 (AGAL-10) Hawkesbury River Sediment.

Sediment pH and solubility study

To determine the effect of different pH on the solubility of metals from the sediment downstream of the discharge a desktop experiment was designed. The experiment part defined utilising the method from Australian Standard Leaching Procedure (ASLP) and part pilot. To determine solubility as a function of pH, sediment from W1 and LDP002 was exposed to solutions of deionised water at pH 8, 7, 6, 5 and 4. To obtain the different pH for each solution a pilot study was conducted. For acidic solutions, nitric acid (HNO₃) was used, as it is also an oxidiser, providing oxidising conditions, replicating those of the river and sodium hydroxide (NaOH) for basic solutions. To determine the quantity of NaOH and HNO₃ and the buffering capacity of sediment, NaOH and HNO₃ was added dropwise into a 1L HDP bottle of deionised water and 50g of sediment from LDP002 and W1. The solution was shaken for 12 hours using an orbital shaker, checking pH every 30 minutes to analyse buffering capacity and add the required amount of NaOH and HNO₃ to maintain the desired pH.

This was completed until the desired quantity of NaOH and HNO₃ was determined and the intervals between when additions were needed to maintain the desired pH.

The method utilised the collected sediment from LDP002 and W1 (Table 2, Figure 6). Sediment was dried at 40°C for 72 hours and sieved down to 2mm using a mechanical shaker as per the ASLP. A subsample of sediment was then analysed using ICP-AES by a National Association of Testing Authorities (NATA) accredited laboratory with 3 replicates and AGAL-10 blanks to determine the baseline concentration of metals in the sediment. 50g of sediment was added into each 1L HDP bottle with screw on lids yields 35 analyses in total (3 replicates for each pH for both LDP002 and W1 and 5 deionised water blanks). 1L of solution was added into each flask (ratio 1 solid: 20 liquid as per ASLP). The lids of the flasks were screwed on loosely to allow for oxygen inflow and oxidation; replicating field conditions. The flasks were then placed on an orbital shaker for 12 hours. Once shaking was completed the solution (resulting leachate) was filtered using a syringe with a 0.45 µm filter and a subsample of 60ml was analysed for dissolved metals. The percentage of metals extracted was then calculated by balancing the quantity soluble in the water compared to the quantity in the sediment prior leaching.

Results

Longitudinal Water Analysis

The discharge from LDP002 is responsible for significant changes to the water chemistry of the Wollangambe River. The pH was highly variable, however always significantly greater than background conditions (Table 3). Reference sites had a mean pH of 5.04 (slightly acidic), compared to circum-neutral to alkaline pH of the discharge point 6.8 to 8.1, within the limits set by of EPL726 (mean 7.45) (Table 3). The pH reduced linearly downstream, dropping to a mean of 6.5, 22km downstream at W4 (Table 3). Similarly, EC was significantly lower at reference sites (mean 27.5 µS/cm). The discharge point had EC 16 times greater at a mean of 426 µS/cm, above ANZECC guidelines of 350 µS/cm, dropping linearly to a mean of 236µS/cm, 22km downstream (Table 3).

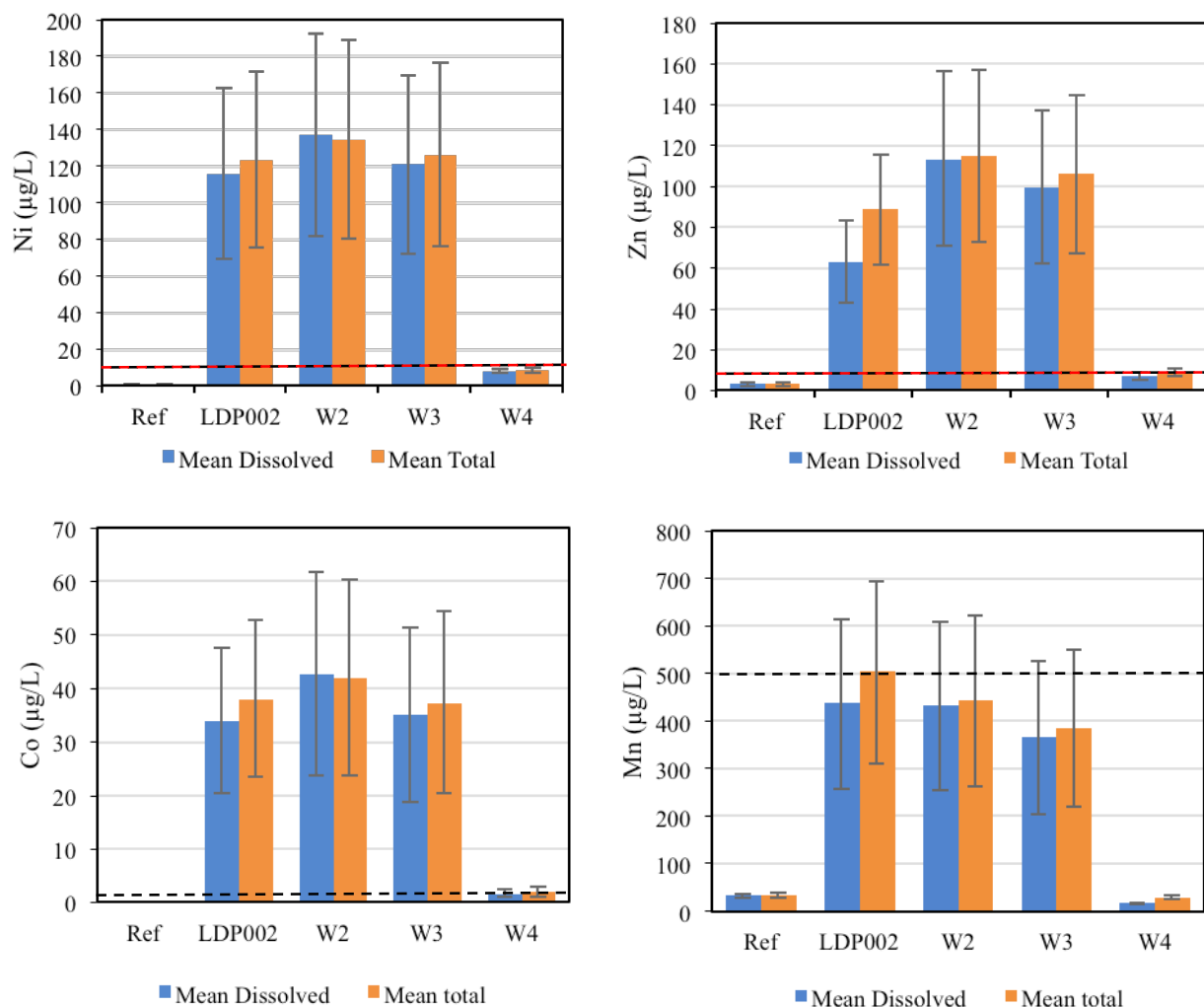
The ionic composition (levels of cations and anions) is significantly higher downstream of the discharge (Table 3). Background conditions had extremely low ionic composition, reporting a mean of 3.8mg/L of Na and 5mg/L of Cl and an absence of Ca and bicarbonates (Table 3). After the discharge point the cations and anions rose significantly over background conditions apart from Na and Cl (Table 3). The cations that reported the greatest increase were Ca (mean 33mg/L) and Mg (11.5 mg/L) and the anions that reported the greatest increase were sulphate (106 mg/L) and bicarbonate (35.5 mg/L) (Table 3). All anion and cations remained well above background conditions 22km downstream of the discharge (Table 3).

Table 3: Summary data of mean pH (including range in brackets), temperature, DO conductivity and ionic composition of the water of the Wollangambe River for each site, including ANZECC 2000 guidelines and EPL726 limits (NG- No guideline, NL – No limit)

		Reference											
		0.2-1.2km below mine						22km below mine					
		Bell Creek, W1		LDP002		W2		W3		W4			
	Analyte	Mean/ Range	ST DEV	Mean/ Range	ST DEV	Mean/ Range	ST DEV	Mean/ Range	ST DEV	Mean/ Range	ST DEV	ANZECC 2000 Guideline	EPL 726
Physiochemical Parameters	pH	5.08	0.24	7.45	0.63	7.22	0.58	7.03	0.5	6.48	0.18	6.5-8.5	6-8.5
		(4.9-5.35)		(6.8-8.05)		(6.6-7.75)		(6.5-7.5)		(6.3-6.65)			
	DO (%sat)	91	2.08	88	1	87	1.15	92	2	91	2.31	90-110	NL
		(89-93)		(87-89)		(87-89)		(90-94)		(90-94)			
	Conductivity	27.58	3.5	425.67	84.11	375	76.54	327	43.58	236	44.58	30-350	NL
(24-31)		(330-488)		(300-453)		(282-369)		(190-279)					
Temperature (°C)	10.5	1.09	16.5	0.87	15	1	13	1.146	10	0.5	NG	NL	
	(9.75-11.75)		(15.5-17)		(14-16)		(12-14.25)		(9.5-10.5)				
Cations (mg/L)	Ca	<0.5	0	33	2	29.5	3.5	29	3	20	1	NG	NL
		0		(35-31)		(26-33)		(26-32)		(19-21)			
	Mg	<0.5	0	11.5	0.5	10.25	0.75	10.15	0.85	7.15	0.15	NG	NL
		0		(11-12)		(9.5-11)		(9.3-11)		(7-7.3)			
	K	<0.5	0	4	0.3	3.15	0.33	3.7	0	2.65	0.05	NG	NL
0		(3.7-4.3)		(3-3.3)		0		(2.6-2.7)					
Na	3.8	0.38	3.4	0.38	3.5	0.1	3.45	0.05	3.7	0.15	NG	NL	
	(3.4-4.3)		0		(3.4-3.6)		(3.4-3.5)		(3.6-3.9)				
Anions (mg/L)	Cl	5	2	3	0	3	0	3	0	4	0	NG	25
		(3-7)		0		0		0		0			
	HCO ₃ ⁻	<5	0	35.5	3.5	30	3	29.5	3.5	20	3	NG	NL
		0		(32-39)		(27-33)		(26-33)		(17-23)			
	SO ₄ ²⁻	<1	0	106	14	51.5	29.38	92.5	17.5	69	2	NG	250
	0	(92-120)		(51.5-110)		(75-110)		(67-71)					

Results indicate that the discharge (LDP002) increases the quantity of metals in the water of the Wollangambe River. Lowest concentrations for all metals except for Fe and Al were seen at reference sites, typical of the sandstone geological setting (Figure 12). Dissolved metal concentration at the discharge was well above those of the reference sites for Ni (116 $\mu\text{g/L}$ mean), Zn (63 $\mu\text{g/L}$ mean), Co (34 $\mu\text{g/L}$ mean) and Mn (437 $\mu\text{g/L}$ mean) (Figure 12). This was significantly above the EPL 726 limits of 11 $\mu\text{g/L}$ for Ni, 8 $\mu\text{g/L}$ for Zn and 2.5 $\mu\text{g/L}$ for Co (Figure 12). The concentration of all metals in the discharge was highly temporal indicated by the error bars (Figure 12). The high level of dissolved metals in the discharge compared to the total indicates that soluble metals are escaping from the treatment, indicating the treatment process failed in meeting the EPL 726 and in preventing the discharge of dissolved metals (Figure 12).

However, the highest quantity of total metals was found at W2. It was also evident that a higher fraction of total metal load was dissolved at W2 compared to LDP002. In fact, almost all the metal load is in dissolved form for Co (mean 42.6 $\mu\text{g/L}$), Ni (mean 137 $\mu\text{g/L}$) and Zn (mean 113 $\mu\text{g/L}$) (Figure 12). This indicates that metals in solid form are being remobilised, most likely in the dam between LDP002 and W2.



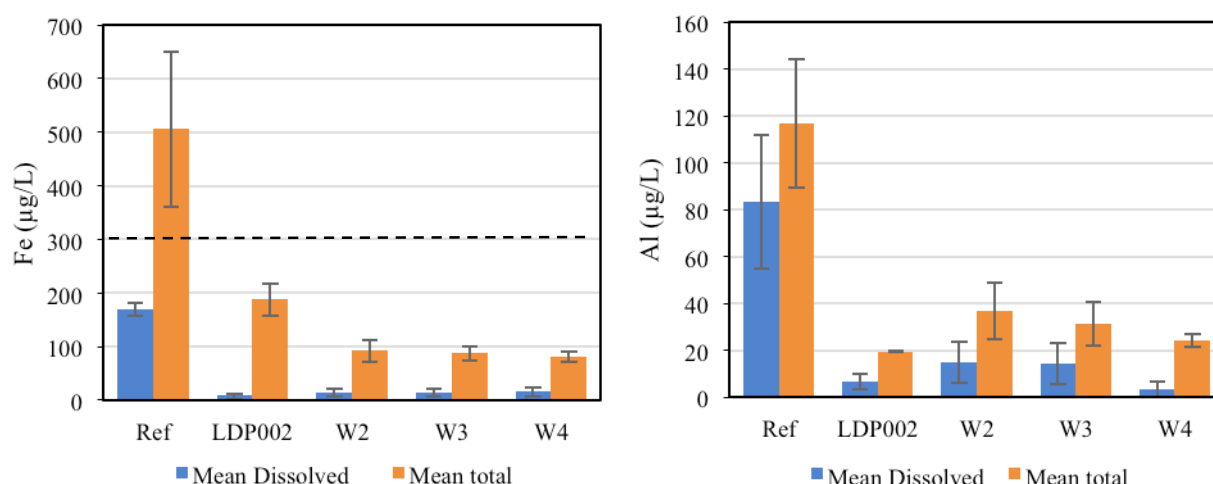


Figure 12: Mean dissolved and total metal concentration of the Wollangambe River. Ni (top left) Zn (top right) Co (centre left) Mn (centre right) Fe (bottom left) and Al (bottom right). Dotted black line represent EPL726 and dotted red line represents ANZECC 2000 Guidelines

2km downstream of the discharge at W3 the concentration of all metals is reduced (Figure 12). For Ni and Co quantities are similar to that seen at the discharge, Zn is elevated above discharge by 20µg/L (dissolved), while Mn shows a linear trend reducing from the discharge (mean dissolved 366 µg/L) (Figure 12). From W2 to 22km downstream at W4 all metals show a significant reduction moving downstream. Mean dissolved Zn at W4 was 7.3 µg/L, just below EPL726 and ANZECC 2000 guidelines of 8 µg/L, similarly mean Ni and Co was found to be 8 µg/L and 17 µg/L respectively (Figure 12). This indicates that the scale of metal contamination spans up to 22km through the GBMWA, often at levels considered to be dangerous to aquatic ecosystems. The concentration of Mn at W4 was like that of reference conditions and Al and Fe were significantly below reference.

Longitudinal sediment analysis

Sediment analyse provided similar results to the water analyses, showing that the discharge significantly increased the quantities of all metals, as well as Ca and S. Like how the highest quantities of Al, Co, Ni and Zn were observed at W2 in the water analysis all analytes for the sediment apart from Fe were highest at W2 (Table 4). For example, mean Zn, Mn, Co and Ni and was measured at 2700 mg/kg, 14500 mg/kg, 1475 mg/kg and 1600 mg/kg respectively at W2 (Table 4). This is significantly above ANZECC guidelines of 200 mg/kg for Zn and 21 mg/kg for Ni of which other metals apart from Pb and Cu are absent in guidelines. This was compared to the mean Zn, Mn, Co and Ni levels at the discharge found at 2550mg/kg, 5200mg/kg, 510mg/kg and 810 mg/kg respectively. This indicates also further potential for remobilisation of metals in the dam

between the two sites. Compared to water, which has highly temporal changes in composition, sediment is less variable, with metals accumulating over time. The result here show that the accumulation has been occurring for an extended period.

Background conditions showed a substantially lower composition of all analytes apart from Al and Fe, which were lowest at W4. Background conditions of Fe and Al are elevated due to the presence of Fe oxides (i.e. limonite, hematite, and magnetite) carbonates (i.e. siderite), and silicates (i.e. chamosite) and aluminosilicates such as kaolinite. However, accumulation of Al and Fe present in the discharge water has also potentially led to increase quantities downstream of the discharge (Table 4).

At W3 all analytes decreased to around that or below what was observed at the discharge. 22km downstream at W4, metals composition still significantly above reference conditions, typically ranging 5-20 times greater (Table 4). Mean Zn was 55.5 mg/kg, Co 67.5 mg/kg, Mn 645 mg/kg and Ni 50.5 mg/kg. Ni was still over two times ANZECC 2000 guidelines (Table 4). Co, Mn, Ca and S appear to persist at elevated quantities compared to different analytes downstream (Table 4). Like the data observed in the water, sediment data indicated the impacts of the mine discharge on sediment quality well extended into the GBMWhA.

Table 4: Summary data of mean elemental sediment composition for each site analysed in the Wollangambe River including range, standard deviation and ANZECC 2000 interim sediment quality guidelines (NG - no guideline)

Sample Analyte (mg/kg)	Reference			0.2-1.2km below mine						22km below mine						ANZECC 2000 Guidelines
	Bell Creek, W1			LDP002			W2			W3			W4			
	Mean	Range	STD DEV	Mean	Range	STD DEV	Mean	Range	STD DEV	Mean	Range	STD DEV	Mean	Range	STD DEV	
Al	2040	1240	538.3	3900	1400	700	6600	8540	4303.6	1950	1900	950	1015	370	185	NG
Sr	2.3	5	2.5	10.5	1.4	0.7	14	10	5	4	4	2	2.5	1	0.5	NG
Ba	10.2	9	4	65	15	7.5	124	93	46.5	56	53	26.5	16.5	3	1.5	NG
Zn	4	4	1.7	2550	1100	550	2700	1900	950.4	560	500	250	55.5	11	5.5	200
Co	4	8	3.1	510	160	80	1475	1250	625	490	440	220	67.5	27	13.5	NG
Cu	4.5	4	1.8	9.5	5	2.5	15.5	13	6.5	5.5	7	3.5	2.5	1	0.5	65
Fe	3485	3800	1756.6	23000	16000	8000	15500	9000	4500	3900	4200	2100	2350	1100	550	NG
Pb	3.17	3	1.3	10.5	3	1.5	13	8	4	5.5	5	2.5	3.5	1	0.5	50
Mn	160	224	100.7	5200	400	200	14500	12000	6450.1	4200	3800	1900	645	150	75	NG
Ni	2.8	4	2.5	810	240	120	1600	1000	500	430	380	190	50.5	1	0.5	21
Ca	100	25	10.8	401	49	25.1	580	7	3.8	450	80	43.6	341	36	19.7	NG
S	88	22	8.5	700	35	17.6	890	40	20	580	70	35	221	22	11	NG

Sediment leaching at different pH

To determine the impact of current pH conditions and potential pH conditions post mine closure on metal leachability, sediment from both W1 and LDP002 were exposed to different pH conditions. Elevated metals observed in the longitudinal study i.e. Al, Co, Ni, Mn, Zn and Fe were targeted in the analysis. Extraction from W1 provided a reference for how the background conditions leached the natural levels of the metals (Figure 13) (Table 5). Ni was absent in the sediment providing no indication of solubility (Table 5). Fe and Al showed similar characteristics with low solubility at pH 5-7 increasing at pH 4 and 8. Mn yielded the highest % of metals extracted. No soluble Mn was observed for pH 8, 7 and 6 (Figure 13). The quantity of soluble Mn increased rapidly from pH 5 to pH 4 (Table 5).

Although the quantity of Zn and Co was low in the sediment, trends in solubility were evident (Table 5). At pH 7 and there was no soluble Zn (Table 5). From pH 6-4 a linear relationship with decreasing pH to increased solubility was observed increasing from 0.02 mg/l at pH 6 to 0.09 mg/l at pH 4 (Table 5). Co was not soluble at pH 8 increasing to 0.02 mg/l at pH 7, which was the same for pH 6 and 5. Solubility increased significantly at pH 4 to 0.06 mg/l (Table 5). Mn yielded the highest % of metals extracted. No soluble Mn was observed for pH 8, 7 and 6 (Figure 13). The quantity of soluble Mn increased rapidly from pH 5 to pH 4 (Table 5).

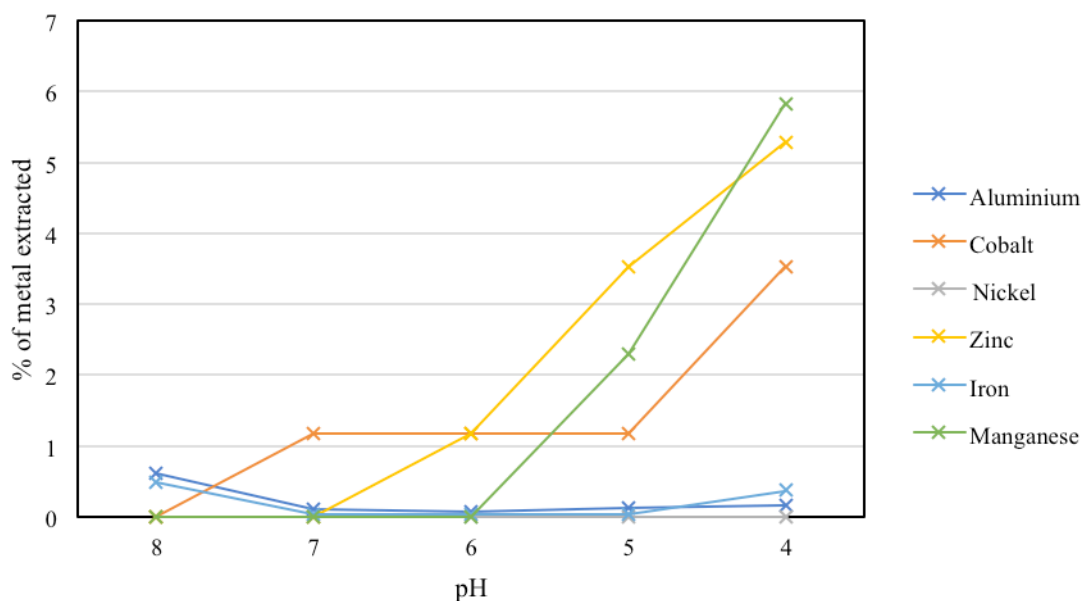


Figure 13: Percentage of total extractable metals at varying pH from W1 sediments

Table 5: pH dependence of metals extracted from W1 (background) sediments with comparison to the concentration of metals in W1 sediment, EPL 726 and ANZECC 2000 Guidelines

Metal	pH					EPL 726 (mg/L)	ANZECC Guidelines (mg/L)	Sediment Concentration (mg/kg)
	8 (mg/L)	7 (mg/L)	6 (mg/L)	5 (mg/L)	4 (mg/L)			
Al	5.6	0.9	0.6	1.2	1.5	No limit	pH >6.5 0.005	913.3
Co	0	0.02	0.02	0.02	0.06	0.0025	No Limit	1.7
Ni	0	0	0	0	0	0.011	0.011	0
Zn	0	0	0.02	0.06	0.09	0.008	0.008	1.7
Fe	8.5	0.63	0.53	0.6	6.4	0.3	No Limit	1733.3
Mn	0	0	0	1.38	3.5	0.5	1.9	60

Sediment from LD002 showed considerably different leaching trends. The quantity of metals was elevated in the sediment as well as levels cations and anions. Like the reference sediments Fe and Al were present in the highest quantities in the sediment, however similarly showed low to no solubility across all pH ranges. The only increase to note was very low solubility at pH 4 and 8 for Al at 0.7 mg/L and 0.8 mg/L respectively (Table 6). Zn showed high solubility, similar to that in the reference sediment. Zn had a high concentration in the LDP002 sediment at 896.7mg/kg (Table 6). Zn began to be soluble at pH 8, however was noticeably soluble at pH 7 at 3.32mg/L (Table 6). Compared to W1 Zn saw an increased dram from pH 7-4 opposed to a linear. At pH 5 30.6 mg/L was leached and 81 mg/L at pH 4, which was 9.03% of the total Zn present in the sediment (Table 6) (Figure 14). Ni showed similar trends to Zn, however was found in lower quantities in the sediment. Ni had a linear increase to pH 5 then increased exponentially at pH 4 (Table 6). Like Zn at pH 8 Ni was soluble in lower quantities. At pH 6 the same % of Ni and Zn was extracted, however at lower quantities i.e. 4.7 mg/L to Zn 11.4 mg/L (Figure 14). At pH 4, 19 mg/L was soluble, which was 5.14 %. Co demonstrated the same trend as Ni, however at lower quantities and % extracted (Table 6) (Figure 14). However, at pH 8 no Co was soluble, becoming significantly soluble at pH 7. At pH 5 1.24mg/L of Co was soluble, increasing significantly at pH 4 to 3.3mg/L (Table 6). Mn showed a low % of extraction compared to the quantity found in the sediment at 1066.7 mg/kg, however was still elevated in the leachate (Figure 14). The % extracted was similar to Co, which was found at 203.3 mg/kg (Table 6). Mn solubility showed a linear relationship with pH decrease. Mn solubility at pH 8 comparable with Zn and Ni at 0.14 mg/L, increasing to 14.4 mg/L at pH 4 (Table 6).

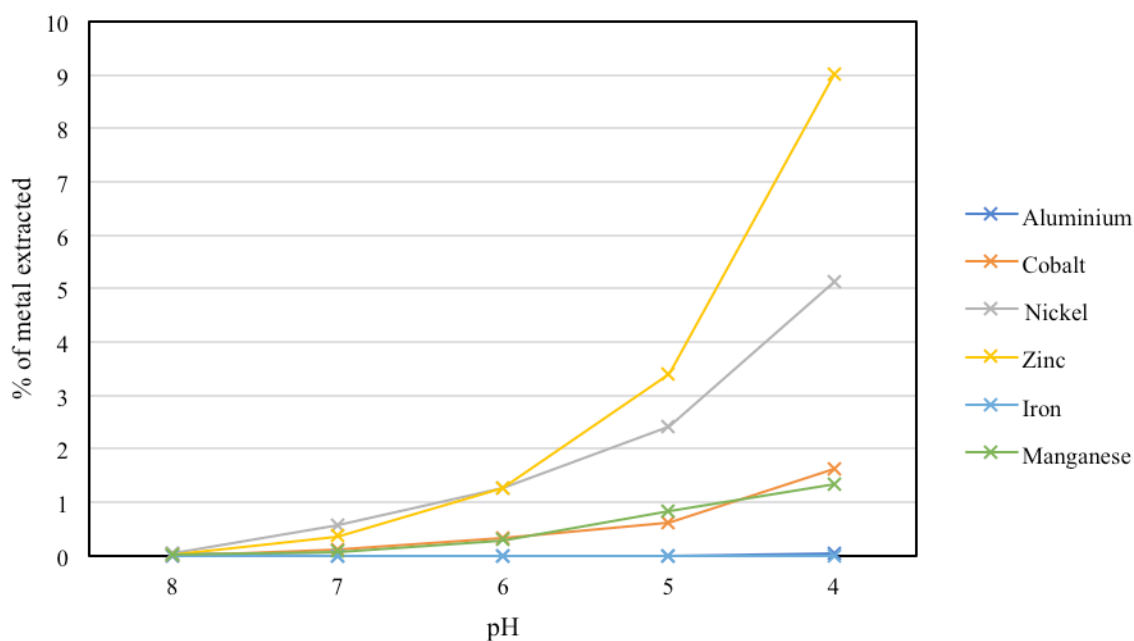


Figure 14: Percentage of total extractable metals at varying pH from LDP002 sediments

Table 6: pH dependence of metals extracted from LDP002 sediments with comparison to the concentration of metals in LDP002 sediment, EPL 726 and ANZECC 2000 Guidelines

Metal	pH					EPL 726 (mg/L)	ANZECC Guidelines (mg/L)	Sediment Concentration (mg/kg)
	8 (mg/L)	7 (mg/L)	6 (mg/L)	5 (mg/L)	4 (mg/L)			
Al	0.8	0	0	0	0.7	No limit	pH >6.5 0.005	1966.7
Co	0	0.24	0.68	1.24	3.3	0.0025	No Limit	203.3
Ni	0.18	2.14	4.7	9	19	0.011	0.011	370
Zn	0.12	3.32	11.4	30.6	81	0.008	0.008	896.7
Fe	0	0	0	0	0	0.3	No Limit	9366.7
Mn	0.14	0.88	3.2	9	14.4	0.5	1.9	1066.7

Discussion

Spatial analysis of water chemistry and metal solubility

This study differs from previous investigations in that it investigates and compares total and dissolved metals in sediment and water. This analysis seeks to identify the mobilisation of metals and relate this to the efficacy of the current treatment system. Results show that remobilisation of metals is occurring as the lime-based alkaline waste water discharge progressively mixes with the naturally acidic surface water of the Wollangambe River (Table 6) (Figure 14).

The licenced discharge from the Clarence Colliery at LDP002 is a high-volume source of pollution (Table 4) (Figure 12) (Jones and Eames, 1996; Cohen, 2002; NSW OEH, 2015; Belmer et al., 2014; Wright et al., 2017). This study reveals consistent data that reaffirms the discharge has a high pH, ionic composition, conductivity, temperature and metals in water and sediment compared to reference conditions (Table 3, 4) (Figure 12). Analysis of both total and dissolved metals indicates that most of metals were found in the dissolved fraction suggesting the treatment system has failed to prevent contamination of the environment (Figure 12).

The comparison of total and dissolved metals in the water and sediment between LDP002 and W2 highlights the significance of the remobilisation process (Figure 12). The quantity of dissolved Zn, Co and Ni noticeably increased (approximately 100% of total metals) between these sites (Figure 12). At W3, 1km downstream from W2, the quantity of metals in water decreased to similar levels found at the discharge LDP002 (Figure 12). The dissolved fraction at W3 also decreased to a percentage just above the discharge for Co (93.8%) and Ni (95.8%) i.e. and was still significantly above discharge for Zn (94%) and Mn (94%) (Figure 12). 22km downstream it was evident that the mine wastewater discharge still had an influence on water and sediment composition, reinforcing the data from prior studies (Table 3, 4) (Figure 12) (Cohen, 2002; Belmer et al; 2014; NSW OEH, 2015 Wright et al., 2017). At W4 metal concentrations in the water were just below ANZECC guidelines for Zn, and Ni, both reporting a mean of 7.5µg/L (Figure 12). Ni concentrations in sediment was 2.5 times above ANZECC 2000 guidelines at 50.5mg/kg (Table 4).

This study identified the sediment of the Wollangambe River as a reservoir of potential source material for the ongoing contamination of the Wollangambe River (Table 4). Metal enriched sediments were found up to, 22km downstream from the discharge (Table 4). The depth of sediment, as a sink zone for the reservoir of metal pollution, varies considerably in the river reflecting geomorphic conditions. While this study did not attempt to quantify the amount of mine related sediment in the river, it is known that sediments act as a sink for pollutants and would represent an environmental legacy issue of the mine long after it closes.

Metal extraction tests revealed that a change in pH from alkaline to acidic conditions will have a significant role in contributing to metal solubility and in turn, likely to contribute to a decline in environmental condition of the river (Table 6) (Figure 14). This may be particularly problematic when the mine closes and is not discharging high volumes of alkaline wastewater when the sediments will be directly exposed to the naturally low pH water. Under these conditions it is anticipated that metal concentrations in the water nearer the mine could be much higher than at present.

Background environmental issues

Natural acidity and buffering capacity

The regional geology also plays a significant role in the natural acidity present as ‘background’ conditions. Surface geology of the region is primarily composed of the Narrabeen Group sandstones, primarily the Banks Wall Sandstone. The sandstone is highly weathered being primarily composed of quartz with iron minerals from oxides in the sandstone and from iron bands seen in the formation of pagodas from differential weathering (Washington and Wray, 2011). Iron minerals include: iron oxides (i.e. limonite, hematite, and magnetite) iron carbonates (i.e. siderite), and iron silicates (i.e. chamosite). Aluminosilicates (kaolinite) are also present in the parent rock material (Boon, 2017; Loughnan et al., 1974; Washington and Wray, 2011).

The soil characteristics reflect the regional geology and have a significantly low buffering capacity. The low buffering capacity means that if additional acidity is introduced, typically via rainfall, the soils will reflect the acidic pH of the rainfall (Boon, 2017). The resulting acidic conditions in the soil, will leach out most of the minerals providing any buffering capacity, further increasing acidity.

Within the study area, the soil pH is generally acidic (pH of 4-6). The inherently low buffering capacity means that the soil, sediment and water are at risk of pH changes upon receiving waters of differing pH, particularly if more acidic. In this case the addition of more acidic conditions via wet or dry acidic deposition or from AMD will contribute to and exacerbate the current acidic conditions in the waterways.

Anthropogenic acidity

Acidic deposition from the Lithgow Power Station (1928-1964), Wallerawang (1957-2014) and Mt Piper (commissioned 1992 and currently in operation) power stations have potentially exacerbated the already low buffering capacity of the soil and in turn the acidification of aquatic environments. The acidic wet and dry deposition is a consequence of the burning of coal that produces SO₂ and NO_x emissions, which react with oxygen and water in the atmosphere to form sulphuric and nitric acids. These acids can be deposited as dry particles and gases. Wallerawang and Mt Piper power stations have previously been identified as a high-volume sources of NO_x and SO₂ (Malfoy et al., 2005). In 2002 Mt Piper produced 1400MW of electricity and emitted a mean of 1153 g/s of NO_x and 1549 g/s of SO₂ (Malfoy et al., 2005). Wallerawang had an annual output of 1000MW and emitted a mean of 791 g/s of NO_x and 1282 g/s of SO₂ (Malfoy et al., 2005).

Ayers et al (1995) analysed the impact of these power plants of deposition of acidic species over 2 years at 4 locations at a radius of 20km away from the central point of the Mt Piper and

Wallerawang Power Stations. One site was located 20km SE of the central point on the outskirts of Lithgow, 5km SSW of Clarence Colliery, with another site located E of the power stations roughly 10km NNE of Clarence Colliery, with the others located SW and NNW of the centre point. The Ayres et al study showed that rainfall at the E and SE site close to Clarence Colliery both had a mean rainfall pH of 4.75. The study, however, indicated that rain water pH wasn't a good indicator alone of acidification. Organic acids contributed to 1/3 of total acidity in this region. Dry deposition and wet deposition was evident at all sites, with dry deposition of S and N exceeding wet deposition of SO_4^{2-} and NO_3^- (Ayers et al., 1995). The study found that the total acid depositions were low compared to American and European coal mine sites, however the long history of coal related emissions in and around Lithgow, from the 1860's, was likely to contribute to regional acidification levels.

Impact of acidity on river chemistry

Background pH conditions of the Wollangambe River is acidic ranging from 4.9 – 5.35 with a mean of 5.08 (Table 3). This reflects the pH of the rainfall and the natural soil acidity. The low buffering capacity is also present in the water analysis where bicarbonate, calcium, magnesium and potassium ions are largely absent or in very low levels (Table 3). The result of the acidity and low buffering capacity is that metals present in the water are often completely dissolved.

Acidity and its implications on metal solubility

Acidity is also an issue on the mine site itself in the production and treatment of acid mine drainage. Treatment involves the use of a conventional lime treatment plant. The use of a lime neutralisation plant, which discharges into an acidic stream, presents many secondary environmental issues.

The performance of the treatment plant, and by reference the EPL, has been critiqued by Jones and Riley (1996), Jones and Eames (1996), Cohen (2002) and Wright et al (2017). The EPL is concerned primarily with end of pipe water quality. However as revealed in this study and by Jones and Eames (1996) and Cohen (2002), secondary remobilisation of metal contaminants is occurring and contributing to a deterioration in the environment. The current study provides a comparison between total and dissolved metals as well as the leachability of contaminants in the sediment at different pH in the river. It concludes that the AMD treatment is not effective at removing some metals, nor is the EPL in managing metal contamination if the longitudinal impacts of the mine on the Wollangambe River are considered.

Value of measuring total and dissolved fraction and sediment

Total metals, include the dissolved and solid form, which do not necessarily reveal the patterns of metal solubility and remobilisation. To assess the spatial and temporal changes of metals in the environment both total and dissolved metal analyse should be undertaken. A case in point is demonstrated in this study; soluble metal concentrations changed significantly between monitoring sites, and even over relatively short distances; The fraction of metal solids, most likely precipitates, is being discharged by the mine is providing potential material for remobilization; Combined these characteristics suggest the treatment system is not addressing the management of metal pollution from a whole of environmental perspective (Table 4) (Figure 12).

Implications of pH on metal solubility within the treatment

The aim of conventional lime treatment is to raise pH to the point that metals become insoluble enabling them to precipitate as hydroxide particles. Just as rising the pH can achieve this change, when pH lowers the process is reversed. Managing metal solubility at the Clarence Colliery has been an issue since conception. Jones and Eames (1996) completed the first comprehensive investigation of the treatment performance reporting high quantities of dissolved metals and Ca were present in both the sediment pond and polishing lagoon. Extraction tests on the sediment revealed that pH plays a significant role in the mobilisation of metals (Figure 9). However, what was not discussed in detail in Jones and Eames (1996) study was the significant quantity of Ca being discharged from the treatment plant into the sediment pond and in turn the polishing lagoon. The Ca levels in sediment within the sediment pond was reported to be 0.38% and in the polishing lagoon was 0.041%. Similarly, Ca was elevated in the water of the sediment pond at 25mg/L and 20mg/L in the polishing lagoon. This indicates that there is a high quantity of metal hydroxides that have potentially entered the polishing and sediment pond.

In pH extraction tests, Ca showed similar patterns to Co, Mn, Ni and Zn, indicating that metal solubility could be associated with the Ca. Similarly, in Tack et al (1996) Co, Ni and Mn solubility in relation to pH was associated with the same patterns as Ca. This concept was further explored in Szarek–Gwiazda (2014) where elevated increases in Cd, Pb and Mn were due to these elements being present in large amounts in carbonate forms in the sediment. This means that as acidification of the sediment occurred this led to the dissolution of carbonates resulting in the release of the associated metals (Buykx et al. 2000).

At Clarence Colliery, the increase in solubility of metals could mean either one of two things or both: (1) the solubility pattern of these metals is like Ca; and or (2) metals bound to Ca as metal

hydroxides from the treatment process are becoming soluble and subsequently releasing these metals into solution.

Analysis of total and dissolved metals at the discharge in this study indicates that most of the metals were in dissolved form, indicating the treatment is not adequately addressing metal pollution. For Zn, Ni, Co and Mn the percentage of dissolved fraction compared to the total was 71%, 94%, 89.7% and 86.9% respectively. Total quantities of Zn and Ni were consistent with the Wright et al (2017) study at 88.68 µg/L and 123.33 µg/L, significantly above ANZECC 2000 guidelines and EPL 726 at 8 µg/L for Zn and 11 µg/L for Ni (Figure 12). It is also important to note that some of the metal fraction was also in solid form (Figure 12). The high quantity of Ca in the LDP002 water (30 mg/L) and sediment (100mg/kg) indicates that precipitated metal hydroxides are potentially being discharged into the river (Table 4) (Figure 12).

Implications of pH on metal solubility after the point of discharge

The remobilisation of precipitated metals in the Wollangambe River was first identified by Jones and Earns (1996). Their study revealed that remobilisation was occurring in the dam between LDP002 and W2. The quantity of metals in the sediment were less than those measured at W2, indicating metals were becoming soluble from the sediments in the dam and depositing downstream at W2. Sediment increased from 7370 mg/kg to 21200 mg/kg for Zn, 1050 mg/kg to 2520 mg/kg for Co, 2510 mg/kg to 5970 mg/kg for Ni, 4565 mg/kg to 14200 mg/kg for Mn and 3900 mg/kg to 6600 mg/kg and 15500 mg/kg to 22500 mg/kg for Al from the dam to W2. This finding was confirmed by Cohen's investigation (2002) who noted that precipitated Mn was escaping into the polishing lagoon, where it became soluble in the lagoon and the Wollangambe River due to the pH being too low. The current study provides further evidence that remobilisation of metals is occurring and is likely to be contributing to the decline in environmental conditions as noted by Wright et al (2017) and Belmer et al (2014).

The comparison between total and dissolved metals in water and sediments indicates the remobilisation of metals between sites LDP002 and W2 (Figure 12). The total quantity of Zn, Co and Ni increased significantly over discharge at W2. More importantly the fraction of dissolved metals increased to 100% for Ni and Co and 98.52% for Zn W2 (Figure 12). This change indicates that the precipitates from the discharge, or metals bound to sediment particles, are being remobilised once entering the waterway. Similarly, the quantity of metals in the sediment increased from 2550 mg/kg to 2700 mg/kg for Zn, 510 mg/kg to 1475 mg/kg for Co, 810 mg/kg to 1600 mg/kg for Ni, 5200 mg/kg to 14500 mg/kg for Mn and 3900 mg/kg to 6600 mg/kg for Al (Table 4).

As noted in the Jones and Earnes (1996) study, pH plays a significant role in the solubility of metals in the polishing lagoon and sediment pond, the same is occurring in the dam and river. As conditions become more acidic solubility increases. At LDP002 the mean pH was 7.45. At W2 just below the dam, pH reduces from 7.45 to 7.22 as the discharge meets the Wollangambe River, mixing the acidic background water with alkaline discharge water (Table 3). The decline in pH is only minor at this point reflecting the limited extent of dilution from the 'normal' flow characteristics of the Wollangambe River. Immediately downstream of the discharge mine, the quantity of natural river is estimated to be less than 1-5% of the total flow, with the balance derived from the mine. Although this pH drop is small (0.2 pH units), the dam significantly slows the flow of water, allowing water to pool, providing a point of residency where the lower pH can react with the sediment and suspended solid metals. This residency at the lower pH could potentially allow for precipitated metals in the discharge and the sediment of the dam to become soluble. Even at the slightly alkaline pH conditions, extraction tests in this study revealed that at pH 8 Zn, Ni and Mn was significantly soluble, measuring 0.12 mg/L, 0.18 mg/L and 0.14 mg/L respectively (Table 6). This indicates the current operating conditions of the mine and its EPL do not prevent remobilisation of metals.

Of greater concern in relation to metal solubility is the gradual and eventual return to naturally acidic conditions. At mean background conditions of pH 5 solubility is significantly increased (Table 6). At pH 5 3.32 mg/L of Zn, 2.4mg/L of Ni, 0.88 mg/L of Mn and 0.24 mg/L of Co were extracted from LDP002 sediments (Table 6). Interestingly Zn and Ni, were identified as being associated with fine and medium grained sands has the largest percentage of metal extracted, while Co was identified as being associated with fine grain material and Mn was associated with biofilm (Cohen, 2002). The lower quantity of Mn extracted makes sense as biofilm was avoided when collecting sediment for extraction tests to prevent skewing of results.

The interaction of pH and metal solubility at the Clarence Colliery discharge site is likely to be a dilemma for the environmental regulators who, to date, rely on the mine to use conventional lime based treatment as the basis for their water and sediment quality control. Past and current EPL conditions set pH levels at the discharge point far greater (pH 6-8.5) than natural conditions. This primarily reflects the operational needs of the lime based treatment system and fails to deliver a treatment train approach that would otherwise enable discharge water to return to the river at similar pH conditions.

Impact of DO conditions on metal solubility

Along with pH being a means for metal solubility, DO levels can also play a significant role. The potential impact of DO on metal solubility at the site was first hypothesised by Jones and Earnes (1996). It was thought that high levels of Zn and Mn in the sediment and polishing lagoon were due to low DO in the sediments, highlighting the need to understand the DO conditions of dam sediments in the river.

Typically, oxidized conditions favour metal insolubility, while reducing conditions favour metal solubility (Miao et al., 2006). However, this is complicated by the presence of sulphides where the opposite occurs, as metals typically are in stable sulphide forms (Pardu and Patrick, 1995). Sulphides can be present in high quantities in coal (e.g. iron sulphides such as pyrite).

The treatment process also complicates patterns of solubility under different DO conditions. Due to the treatment process, metals Zn, Co, Ni and Al co-precipitated with iron and Mn (Figure 8). Metals co-precipitated with Fe and Mn, theoretically could become soluble following reduction, which could also happen in the dam (Harrington et al., 1998). Although surface water is usually high in DO, this does not reflect the DO of the dam sediment, which is more likely to be under anoxic conditions. Determining the current state of the metals (i.e. as hydroxides, sulphides or bound to sediment particles) will be beneficial. Through understanding DO conditions in the dam and the current state of metals, the environmental conditions could be replicated in extraction tests for both pH and DO this would help; (1) Determine if DO levels are contributing to metal solubility in the river; and (2) Replicated DO conditions in extraction tests for dam sediments to determine the effect of pH on solubility from the sediments in the dam.

Implications of study on licencing and management of the site

By virtue of the treatment process approved as part of the mine's development consent and EPL, the mine discharge and remobilisation of metals in stream will likely continue to contaminate the Wollangambe River for a long time. The contamination will extend beyond the life of the mine as a consequence of remobilisation of metals from mine related sediments already in the river (Table 1). This study, and others, point clearly towards a more rigorous need for EPL process that considers the impact of contamination, including secondary pollution associated with changing physio-chemical processes. Further, the study reveals the value of sediment, when compared to water alone, as a better long-term indicator of contamination including its utility to quantify the 'sink' of contamination that may arise from a mining or other activity. The measurement of contaminants in sediment has recently been introduced into EPL 726 as part of the 'Wollangambe River

Environmental Monitoring Program’. This is a step forward in the monitoring of the site as concentrations of pollutants in the mine waste water, that can be highly variable, are used to set the permissible discharge limits contained in the EPL (Table 1) and in turn direct the type of water treatment used by the mine.

Added to the complexity of regulating pollution from this mine is how the ANZECC guidelines are followed and incorporated into the EPL (Table 1). While the ANZECC guidelines support locally based catchment studies and information to determine what is ‘acceptable’, the use of default limits often overrides informed and locally based studies. In this instance, the problem of discharge of alkaline water into a naturally acidic stream is a clear example. This licence standard clearly does not address secondary pollution arising from the remobilisation of metals as pH returns to its naturally acidic state. Guidelines are also incomplete e.g. sediment quality guidelines are available for 9 metals in ANZECC guidelines. Potentially toxic metals such as Co are missing from both water and sediment guidelines (Table 1). Without these metals in guidelines, policy makers don’t know how to deal with them, typically using overseas guidelines e.g. Canadian guidelines for Co in EPL 726.

This study has revealed the significant longer-term and spatially distributed environmental implications of contaminated sediments, which have already deposited in the river from the mining operation. The discharges impact on sediment composition is now only just being recognised under the EPL. The EPA is silent from the impacts of the discharge on sediment composition post discharge as the POEO (1997) act states that the licence only protect the company from prosecution for discharging contaminants as listed on the EPL. This means that EPL doesn’t permit these impacts. As part of the WREMP sediment is now being monitoring. This shows an improvement in moving towards a positive outcome for the sites. Through the WREMP, prior studies (Jones and Eames, 1996; Cohen, 2002; NSW OEH, 2015; Belmer et al., 2014; Wright, 2017) and the current investigation, the scale of remobilisation and pollution can be determined, leading to site specific pollution limits for total and dissolved metals and sediment composition for the site. This will most likely required a changed in the treatment process and works to remove sediment primarily from the Wollangambe dam to prevent remobilisation of these sediments post mine closure.

Conclusions: future research and key developments of the study

This study has provided evidence of the significant remobilised metals from the Clarence Colliery. The conventional lime based treatment, as used by the mine, fails to adequately remove metals as the alkaline discharges returns to its natural acidic state and in doing so, remobilising metals into the environment. These results highlight the limitations of the traditional lime based treatment

process and points to the need for a treatment train approach that is reflective of the naturally acidic receiving environments. It points to an inadequate attention of AMD and its treatment with the physio-chemical setting as part of the planning consent and subsequent pollution licencing. The study fills a gap in the environmental management literature with respect to the impacts of treated AMD and natural acidic streams.

In revealing the implications of the remobilisation of metals post treatment, the study points to the need to further understand the legacy issues associated with the contaminated sediments already in river and those that are likely to be permitted to be discharged as part of the EPL. This is likely to create an ongoing environmental problem for the Wollangambe River well past the closure of the mine and an aspect that should be foremost in the consideration of the environmental and mining regulators as part of the mine closure process.

The study has identified that the conventional lime treatment system itself may also be contributing to the metal pollution by way of the physio-chemical characteristic occurring in the dam downstream of the discharge. Further exploration and research is needed to understand whether reducing conditions are operating within the dam and the quality of sediments therein, that may further exacerbate metal solubility alongside the described changes in pH.

Additional research on extraction methods and modelling of metal pollution should be completed at the site. pHstat should replace the current method of extraction as per the benefits stated on pg. 20. There is value in improving the spatial extent of samples extracted as well as the method of extraction. To provide an indication of how pH will impact metal solubility throughout the whole river, samples from W2, W3, a site between W3 and W4, and W4 should be examined as well. This will provide an indication of how pH is impacting the solubility of metals downstream and to what extent a total load of metal contamination can be estimated.

Understanding the mineralogy and speciation of the metals in the river will be beneficial in determining their solubility behaviour in relation to pH and DO as well as any changes in mineralogy pre- and post-remobilisation. The use of techniques such as IC-ICP-MS, ICP-AES and ETAAS, could provide speciation of metals, determining if they are present as hydroxides and sulphides and XRD will give an indication of other major minerals present. This will provide key information on the behaviour Ca, in relation to metal hydroxides as well as metals sulphides in extraction tests, help to clarify the pathways of metal solubility in the river. Together with all the other methods mentioned here, a full picture of the contamination in the river and its response to pH and DO can be determined.

This study has investigated the influence of naturally acidic stream waters on metal solubility within the Wollangambe River. There are many other coal mines in the greater Sydney region where such conditions and EPLs are potentially contributing to a long term environmental issue. The study affirms the need for greater attention by environmental planners, regulators and the scientific community to understand the site-based implications of AMD and treatment particularly, in naturally acidic streams.

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End.

Appendix

Appendix 1: Raw data for table 3

	W1/Bell Ck	LDP002	W2	W3	W4
pH	5.35	8.05	7.75	7.5	6.65
	4.9	6.8	6.6	6.5	6.3
	5	7.5	7.3	7.1	6.5
DO	93	89	89	94	90
	92	87	87	90	90
	89	88	87	92	94
Conductivity	27.75	459	372	330	239
	24	330	300	282	190
	31	488	453	369	279
Teperature	10	17	14	12	10
	9.75	17	15	13.5	9.5
	11.75	15.5	16	14.25	10.5
Calcium	<0.5	35	33	32	19
	<0.5	31	26	26	21
	<0.5	33	29.5	29	20
Magnesium	<0.5	11	11	11	7.3
	<0.5	12	9.5	9.3	7
	<0.5	11.5	10.25	10.15	7.15
Potassium	<0.5	3.7	3.8	3.7	2.7
	<0.5	4.3	3.6	3.7	2.6
	<0.5	4	3.15	3.7	2.65
Sodium	3.5	3.4	3.5	3.45	3.7
	3.5	3.4	3.4	3.4	3.9
	3.4	3.4	3.6	3.5	3.6
Chlorine	3	3	3	3	4
	4	3	3	3	4
	6	3	3	3	4
Bicarbonate	<5	35.5	30	29.5	20
	<5	39	33	33	23
	<5	32	27	26	17
Sulphate	<1	106	51.5	92.5	69
	<1	92	76	75	67
	<1	120	110	110	71

Appendix 2: Raw data table 4

Sample	Al	Sr	Ba	Zi	Co	Cu	Fe	Pb	Mn	Ni	Ca	S
LDP002	3200	10	57	2000	430	7	15000	9	5400	690	380	705
LDP002	3900	9.6	66	2559	510	9.5	23000	10.5	5200	810	429	685
LDP002	4600	11	72	3100	590	12	31000	12	5000	930	395	720
W2	9200	19	170	3600	2100	22	20000	17	21000	2100	582	890
W2	660	14	124	2700	1475	15.5	15500	13	14500	1600	576	870
W2	4000	9	77	1700	850	9	11000	9	8100	1100	583	910
W3	2900	6	82	810	710	9	6000	8	6100	620	400	545
W3	1950	4	56	560	490	5.5	3900	5.5	4200	430	470	580
W3	1000	2	29	310	270	2	1800	3	2300	240	480	615
W4	1200	3	18	61	54	3	2900	4	570	51	345	221
W4	1015	2.5	16.5	55.5	67.5	2.5	2350	3.5	645	50.5	341	210
W4	830	2	15	50	81	2	1800	3	720	50	377	232
Bell Ck	530	<1	8	3	2	2	2600	2	79	1	90	78
Bell Ck	460	<1	7	2	2	1	2300	2	66	1	110	91
Bell Ck	720	<1	6	3	10	1	3300	2	290	1	91	70
W1	1600	4	15	6	4	5	6000	5	230	6	112	78
W1	1700	5	15	6	4	5	6100	5	230	6	104	85
W1	1100	2	10	4	2	3	2900	3	67	2	115	92

Appendix 3: Raw data figure 12

	W1/Bell Ck	LDP002	W2	W3	W4
Zinc Total	1.75	35	31	29	6
	3	110	150	140	9
	5	121	164	149	12
Zinc Dissolved	1.75	23	28	25	5
	3	81	150	130	6
	5	85	162	144	11
Nickel Total	0	28	28	26	6
	0	160	170	170	9
	1	182	206	183	11
Nickel Dissolved	0	24	27	24	6
	0	150	180	160	8
	1	174	204	179	10
Cobalt Total	0	9	6	4	1
	0	49	54	48	1
	0	56	66	60	4
Cobalt Dissolved	0	7	5	3	1
	0	45	58	45	1
	0	50	65	57	3
Manganese Total	27	120	100	76	21
	32	670	520	440	30
	43	720	710	640	35
Manganese Dissolved	26	81	96	65	12
	32	590	500	420	17
	39	640	700	615	21
Iron Total	290	130	55	62	62
	780	210	100	93	81
	450	225	123	109	97
Iron Dissolved	170	0	0	0	0
	190	10	19	21	26
	150	15	25	23	22
Alluminium Total	170	20	60	50	20
	100	20	20	20	30
	80	19	30	25	23
Alluminium Dissolved	140	10	30	30	0
	60	0	0	0	0
	50	10	15	13	10