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**An Assessment of the Revegetation Potential of Base-Metal Tailings
from the Tui Mine, Te Aroha, New Zealand.**

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at Massey University

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Abstract

The overall objective of this study was to investigate the revegetation potential of abandoned base-metal (Cu-Pb-Zn) tailings at the Tui mine site near Te Aroha, New Zealand. An estimated 100,000 m³ of sulphide-rich tailings are the legacy of a once prosperous mining venture conducted at the site between 1967 and 1974 by the now defunct Norpac Mining Ltd. The oxidation of remnant sulphides, which constitute as much as 15% of the tailings by weight, has prevented plants from colonising the tailings for more than 20 years and resulted in the formation of Acid Mine Drainage (AMD) which continues to degrade ground and stream waters in the vicinity of the dam.

This study focused on characterising the physical and chemical properties of the tailings in terms of their plant growth potential using a variety of techniques including; Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectrometry (EDS), Flame Atomic Absorption Spectrometry (FAAS), X-ray diffraction (XRD) as well as field based observations and standard laboratory analyses. A long term incubation experiment (carried out over a 1½ year period) and two plant growth trials were also conducted to investigate the ability of liming materials and/or organic waste to ameliorate the tailings in order to provide a suitable growing medium for plants.

The research indicated that, whilst the tailings do not exhibit any major physical limitations to plant growth, chemically the tailings are an extremely hostile plant growth medium. The surface tailings exhibited variable but generally very low pH (2.76 - 3.85) and high concentrations of potentially phytotoxic elements including As (254 mg/kg), Cu (26-991 mg/kg), Pb (1503-27416 mg/kg) and Zn (123-2333 mg/kg). The high availability of these and other metals, including Al and Fe, under the acidic conditions prevailing in the tailings, were identified as the primary factors currently inhibiting plant growth.

The distribution of heavy metals, sulphate and total sulphur with depth indicated that the surface tailings (0-200 mm) have been extensively weathered since their deposition and contain relatively low concentrations of most heavy metals compared to subsurface

tailings. An assessment of the Acid Generating Potential (AGP) of the tailings, using both static and kinetic tests, similarly indicated that the surface tailings have a comparatively low ability to generate acidity by sulphide oxidation. The application of lime at a rate of about 50 Mg CaCO_3 /ha is calculated to theoretically prevent the surface tailings from reacidifying. Below 200 mm depth, however, the AGP is appreciably higher (>140 Mg CaCO_3 /ha) and concentrations of both total and labile (0.1M HCl extractable) Cu, Fe and Zn were found to increase substantially, reflecting an increase in the abundance of chalcopyrite (CuFeS_2), pyrite (FeS_2) and sphalerite (ZnS) and sulphates with depth. The presence of high concentrations of acid-generating sulphide minerals (primarily pyrite) at shallow depths has important implications in that revegetation of the tailings should be based on techniques that minimise the exposure of the largely unweathered, sulphide-rich, subsurface tailings.

The results obtained from the plant growth trials indicated that, on tailings treatments sown with metal-tolerant varieties of *Festuca rubra* or *Agrostis capillaris*, satisfactory cover was achieved upon the addition of lime at a rate of 16.5 Mg/ha or composted sewage sludge at rates >220 Mg/ha. These metal-tolerant plants were found to out yield their non-metal-tolerant counterparts on the limed treatments by as much as 4 and 10 times, respectively. Although vegetation was successfully established on Tui tailings treated with lime, dry matter yields were relatively low compared to treatments receiving high rates of sludge. The growth of all plant taxa was found to significantly decrease where very high rates of lime (112 Mg/ha) were added due to pH-induced nutrient deficiencies.

Results obtained from both the plant growth trials and the lime incubation experiment indicated that the application of low rates of lime and/or sludge (8.25 and 110 Mg/ha respectively) were ineffective at creating a suitable plant growth medium and, in fact, exacerbated growing conditions within a few weeks of application by increasing the availability of labile (0.1M HCl extractable) metals.

The findings of this study indicated that the use of amendments may provide a relatively inexpensive way of facilitating the establishment of plants on the tailings at the Tui mine site. It is envisaged that, at the very least, a vegetative cover will improve the aesthetic appearance of the site and at best reduce AMD by creating an oxygen-depleting, organic-rich cover which may ultimately facilitate the establishment of native species from the adjacent forest.

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CHAPTER 1

Thesis Introduction

1.0 Introduction

‘I walk in the way of Nature, till anon I shall fall and be at rest, yield up my breath to that element from which I draw it day by day, and sinking into that same earth that gave my father his seed, my mother her blood, and my nurse her milk; that earth that has given me food and drink for many a year, and borne with me while I trampled her underfoot and abused her at will.’

Perhaps never in the history of humanity have the words of the Roman philosopher Marcus Aurelius¹ (121-180 AD) been so poignant. Environmental degradation of soils resulting from phenomena such as mining, deforestation, intensive chemical-based agriculture, salinisation, over irrigation and desertification is occurring worldwide at a catastrophic rate (Hillel, 1992). This degradation is ultimately being driven by a continuous and accelerating increase in population and resource exploitation. Thus, at the very time the human population is proliferating, it is becoming increasingly evident that our poor treatment of the Earth and its soil resources is diminishing its capacity to support us (Hillel, 1992).

Although on a global scale environmental degradation resulting from both active and abandoned mine sites is small, it is an extremely serious problem facing many regions around the world and its localised impact on communities and the environment can be devastating. Bradshaw & Chadwick (1980) estimated that about 0.2% of the landmass in the US and 0.4% of the landmass in Great Britain has been seriously impacted by past and present mining operations. In Canada, ever-expanding tailings dams cover more than 50,000 ha of land (Ritcey, 1989). Compared to many countries New Zealand has been little impacted by mining activity. Whilst mining was a mainstay of the New Zealand economy during the early days of European settlement, it is estimated that less than 0.02% of the country's land area has been disturbed by mining. Most of this

¹ Cited in Bradshaw & Chadwick (1980).

degradation was caused by ‘early’ alluvial gold mining operations in the South Island on land generally hosting soils of moderate to low versatility (Fricker, 1986).

Over the past few decades, the introduction of modern mining techniques and high-capacity processing plants has seen a dramatic increase in the potential for mining operations to damage the environment. Rising gold and oil prices during the 1970’s and 1980’s resulted in a worldwide resurgence in mining activity for both coal and gold. Many of the larger current mining operations involve the daily displacement of many thousands of tonnes of rock and the generation of huge volumes of wastewater and tailings. Fortunately attitudes towards mining and mining practices have also changed substantially over the same time period (Ritcey, 1989). As awareness of the potential impacts of mining has grown, so too has the pressure from the public and regulatory agencies on mining companies to minimise environmental impact. Much of the impetus for new mining legislature has stemmed from peoples’ realisation that the world’s resources are finite and that soil is not a readily renewable commodity but rather a complex biological ecosystem and ultimately a precious resource (Bradshaw & Chadwick, 1980).

New legislation and cooperative efforts between industry, regulatory authorities and research organisations have resulted in considerable progress being made towards creating a more ‘environmentally responsible’ global mining industry. Mining legislation in most countries now requires mining companies to implement measures before, during and after operations to safeguard the environment. Mining practices, for example, now commonly try to ensure that the exposure of sulphide bearing wastes is minimised, fugitive dust, noise pollution and silting of water ways is controlled and that the burial of soil materials and the disruption of communities, natural ecosystems, water courses and aquifers is avoided where ever possible. Thus, nowadays most mining operations (particularly in the First World) are conducted in an environmentally and sociably ‘responsible’ manner. The same, however, can not be said of the majority mining operations of yesteryear or of some operations currently being conducted in Third World countries.

Many mining operations conducted prior to the early to mid 1970's were often carried out with little or no regard for potential environmental impact. The lax attitudes towards rectifying environmental damage or reclaiming mine sites were driven, at times, by greed and complacency but more often as a result of lax governmental legislation which was based on ignorance of the processes and potential problems associated with mining.

The Tui base-metal mine site near Te Aroha, New Zealand provides a graphic example of the potential hazards that are associated with many metalliferous and coal mining operations and forms the focus of this thesis. Major mining operations were commenced at the site during the 1960's at a time when legislation in New Zealand governing mining was antiquated and primarily aimed at the promotion of such activities rather than at environmental protection (Fyson, 1991). Few environmental constraints were thus in place to curb the activity of the mining company operating at Te Aroha or to protect the integrity of the surrounding aquatic and terrestrial ecosystems.

Whilst the Tui mine site exhibits a unique character in terms of its mining history, operational practices, geology, climate, hydrology, topographical setting, flora and fauna, many of the problems encountered at the site are common to abandoned mine sites where sulphidic minerals have been mined and/or exposed during operations. The most serious problems at the Tui mine site stem from the exposure of finely ground tailings which contain high concentrations of remnant sulphide minerals capable of generating acidity and liberating base-metals. Not only has sulphide oxidation acidified the tailings and prevented vegetation from colonising the tailings dam, it has also resulted in the degradation of surface and ground water via the generation of severe Acid Mine Drainage (AMD).

The Tui mine site is without question a 'thorn in the side' of the New Zealand mining industry. It is continually cited by environmentalists and anti-mining groups alike as a graphic example of why the mining of 'non-essential' commodities should be discontinued in the Coromandel and elsewhere within New Zealand. Few people will argue, however, that the notoriety of the Tui mine truly reflects the impact that the site has had on the environment. When looked at in context of the country as a whole the effects of the Tui mine are really very localised and effect few people.

In spite of its comparatively small regional impact, it is clear that something must be done to reclaim the Tui mine site. Drainage from the site continues to pollute local streams and at least ethically impact the lives of Te Aroha people. Whilst some consider the tailings dam to be a curiosity, most consider it to be an ‘eyesore’ in the middle of scenic native bush; an unsightly reminder that mining should never have been conducted in such a fragile (and in many senses hostile) environmental setting. It is evident that after more than 20 years mother nature and time have made little headway in ameliorating environmental degradation at the Tui mine site. Unless geological time is left to play its role, human intervention will be necessary to remedy or at least ‘kick start’ recolonisation of vegetation at the site.

The science of land reclamation in New Zealand is still very much in its infancy. Whilst many researchers have gained considerable expertise with respect to implementing reclamation strategies for current, well-planned mining operations, expertise and research into the reclamation of highly degraded abandoned mine sites is relatively scarce. Sites where the processes of sulphide oxidation and acid mine drainage are well established are notoriously difficult to reclaim. This is particularly the case where few resources are available for the implementation of tried and proven (but often prohibitively expensive) reclamation strategies. This study was seen as a ‘golden’ opportunity to increase the reclamation knowledge base within New Zealand and to further global understanding of mine reclamation in different and unique environmental settings.

1.1 General Objectives of Study

Prior to this study, no comprehensive examination had been conducted to investigate the option of revegetating the Tui mine tailings. It was envisaged that this study would:-

- Determine the potential for establishing a vegetative cover on the Tui tailings.
- Provide groups potentially interested in reclaiming the Tui mine site, or similar sites, with useful data that would form the basis of well informed and practical reclamation strategies.
- Elucidate the processes and problems associated with the revegetation of polysulphidic mining wastes.

1.2 Specific Objectives of Study

Specifically this study was aimed at:-

- Characterising the physical and chemical properties of the Tui tailing to identify what limitations are currently prohibiting plants from colonising the tailings.
- Assessing the total and labile metal concentrations of the tailings and their Acid Generating Potential (AGP) to identify tailings material most suited for use as a growing medium for plants.
- Identifying the primary mineral constituents of the Tui tailings and the depth and degree to which the tailings have oxidised.
- Investigating the feasibility of establishing plants in Tui tailings amended with lime and/or organic wastes.
- Identifying ‘optimal’ amendment rates for preventing reacidification of the tailings and facilitating satisfactory plant growth.
- Assessing the performance of several plant species, including a legume and two commercially cultivated metal-tolerant grass varieties, to identify potentially suitable taxa for revegetating the tailings.

1.3 Implementation of Objectives

The objectives of this study were implemented by the combined use of:-

- Field and laboratory-based analysis and experimentation.
- Plant growth trials conducted on disturbed tailings samples in the controlled environment of a glasshouse.
- A lime incubation trial designed to monitor the effectiveness of lime amendments at preventing reacidification.

1.4 Thesis Layout

This thesis comprises eight chapters including the present introductory chapter. The following chapter (**Chapter 2**) provides a description of the information relevant to the experimental site such as its history, geological setting and climate. **Chapter 3** reviews literature pertaining to land reclamation and outlines techniques and cases studies of mine reclamation practices commonly used both here in New Zealand and abroad. **Chapter 4** reports on the results of physical and chemical characterisation of the tailings

and discusses factors pertaining to the tailings' plant growth characteristics. **Chapter 5** presents the results of XRD and SEM work undertaken to elucidate the mineralogy of the tailings and morphological and geochemical trends with depth. **Chapter 6** reports the results of a lime incubation experiment designed to assess the reactivity of tailings treated with various rates of lime in terms of their potential to generate acidity. The penultimate chapter (**Chapter 7**) reports on the results of two plant growth experiments that were conducted simultaneously to investigate the efficacy of lime and organic amendments to ameliorate the tailings plant growth properties. Finally, **Chapter 8** summarises the findings and conclusions of the research presented in this thesis and discusses the opportunity and potential direction for further research at the Tui mine site in particular and at other sites similarly impacted by mining activity and geochemical weathering processes.

CHAPTER 2

Tui Mine Site - Study Area

2.0 Introduction

The aim of this chapter is to describe the study area in terms of its location, vegetation, climate, hydrology, geology, mineralogy, soils and history. Previous research investigating the impact of the Tui mining operation on surface and ground water quality is summarised and discussed in section 2.4. Further discussion of the Tui mine site's impact on the environment is presented in Chapter 3 (section 3.2.2.8).

This chapter discusses each of the physical characteristics of the study area and concludes with a brief section discussing the past laws under which the Tui Mine operated, together with a brief overview of the political issues currently pertaining to the site including ownership and responsibility.

2.1 Location \ Physiography

The Tui mine site (NZMS 260 T13515055) is located on the NW flank of Mount Te Aroha, approximately 3 km NE of the township of Te Aroha (Figure 2.1). This small rural township is nestled at the base of Mt. Te Aroha which forms a part of the Kaimai ranges and dominates the landscape, towering some 952 m above the Hauraki plains. Te Aroha is located approximately 110 km SE of Auckland city and 25 km from the coast on the southern periphery of the Hauraki Goldfield, an area that was extensively prospected and mined during the late 19th and 20th Centuries (Main, 1979). Te Aroha township (population c. 3,500) acts as a service centre for the Thames Valley region whose primary industries include high production dairying, maize, pip and berry fruit production (McLauchlan, 1989).

The physiography of the Hauraki Goldfield is characterised by the generally rugged and steeply-dipping topography of the Coromandel and Kaimai Ranges. These Ranges are dissected by a multitude of streams and creeks, including the Tui and Tunakohoia streams that flank the Tui mine site. Both of these streams have been severely impacted by past mining activity at the site (Tay, 1980; Pang, 1992). The Tui and Tunakohoia

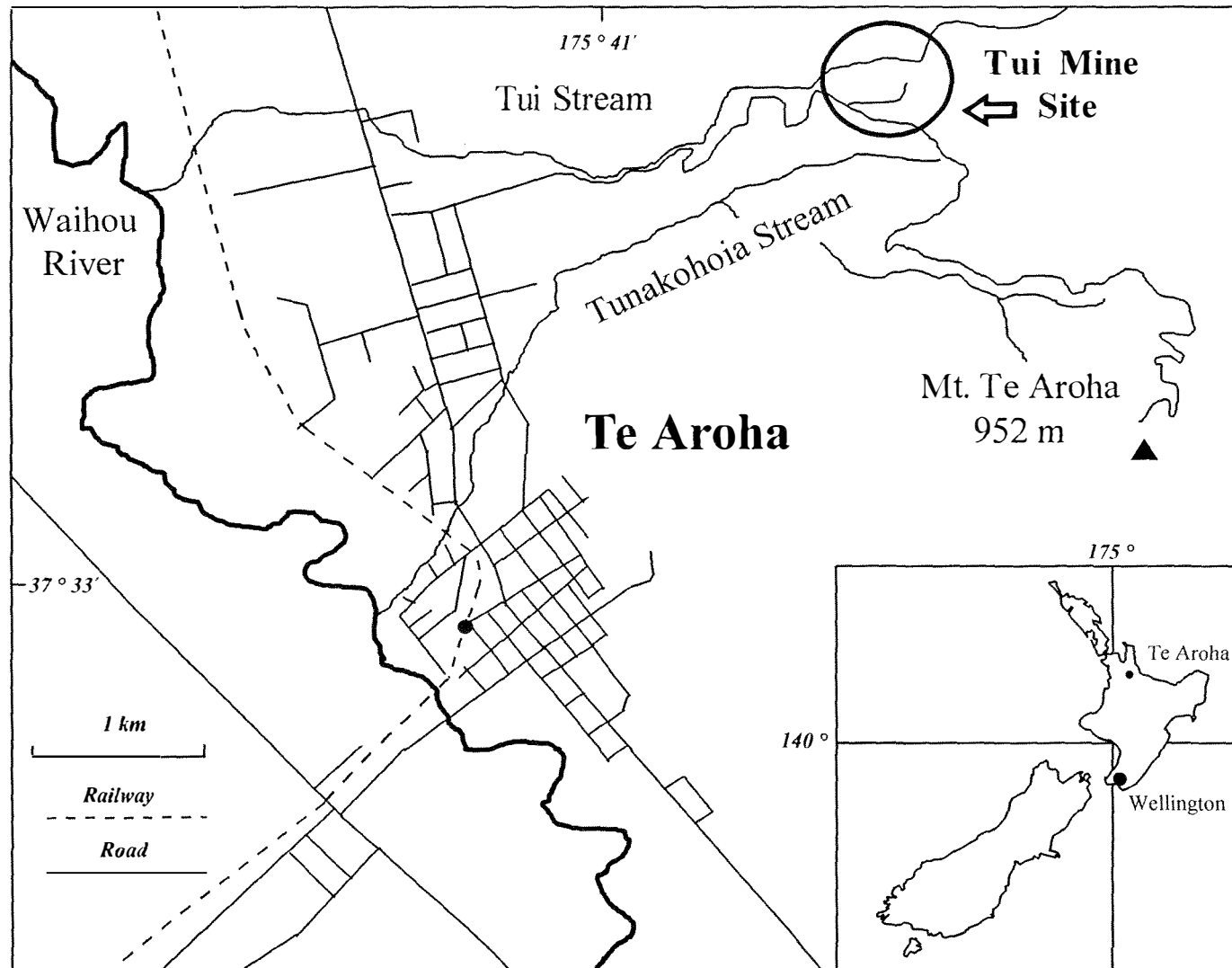


Figure 2.1 Location of the Tui mine site, Te Aroha, New Zealand.

streams are tributaries of the Waihou River, a slowly flowing river that meanders its way north into Thames Estuary along the eastern margin of the Hauraki Plains.

The low-lying Hauraki Plains form a part of a large tectonic feature, about 20 to 30 km wide and over 220 km long, called the Hauraki Depression (Hochstein & Nixon, 1979). North of Waitoa the Hauraki Plains generally stand only a few metres (m) above sea-level. Before extensive flood control measures were implemented the Plains were regularly inundated with flood waters from local streams, the Waihou and Piako rivers, and occasionally by tidal waters. South of Waitoa the surface elevation of the land gradually increases to a few tens of metres and the alluvial surface becomes increasingly dissected and eroded (Hochstein & Nixon, 1979). The northern tract of the Hauraki Depression is occupied by the Firth of Thames, a shallow marine body typically less than 35 m deep.

The Tui Mine consists of a series of underground shafts and adits which lie at altitudes of between 500 and 600 m. Although the land adjacent to the mine adits is degraded, the most obtrusive feature of the site and the focus of this study is a rudimentary dam containing an estimated 100,000 m³ of base-metal tailings (Plate 2.1). The tailings dam is located at an altitude of approximately 350 m on a gently sloping area of land that was previously known as 'Fern Flats' (Cochrane, 1969). Although the mine tailings have largely de-watered, saturated zones still persist adjacent to the confining valley slopes where the water table remains at, or close to, the tailings surface throughout much of the year¹.

2.2 Vegetation

Due to the varying topography and the effects of introduced fauna, past mining and logging operations, considerable variety is seen in the age and type of vegetation on Mt. Te Aroha (Bollard, 1991). While a number of vegetation types, including exotic forestry, pasture and even small areas of virgin forest can be found on the mountain's slopes, the majority of the land above 200 m altitude, including that surrounding the tailings dam, is covered with dense, secondary native bush.

¹ See discussion in Chapter 4 (section 4.2.1.1)

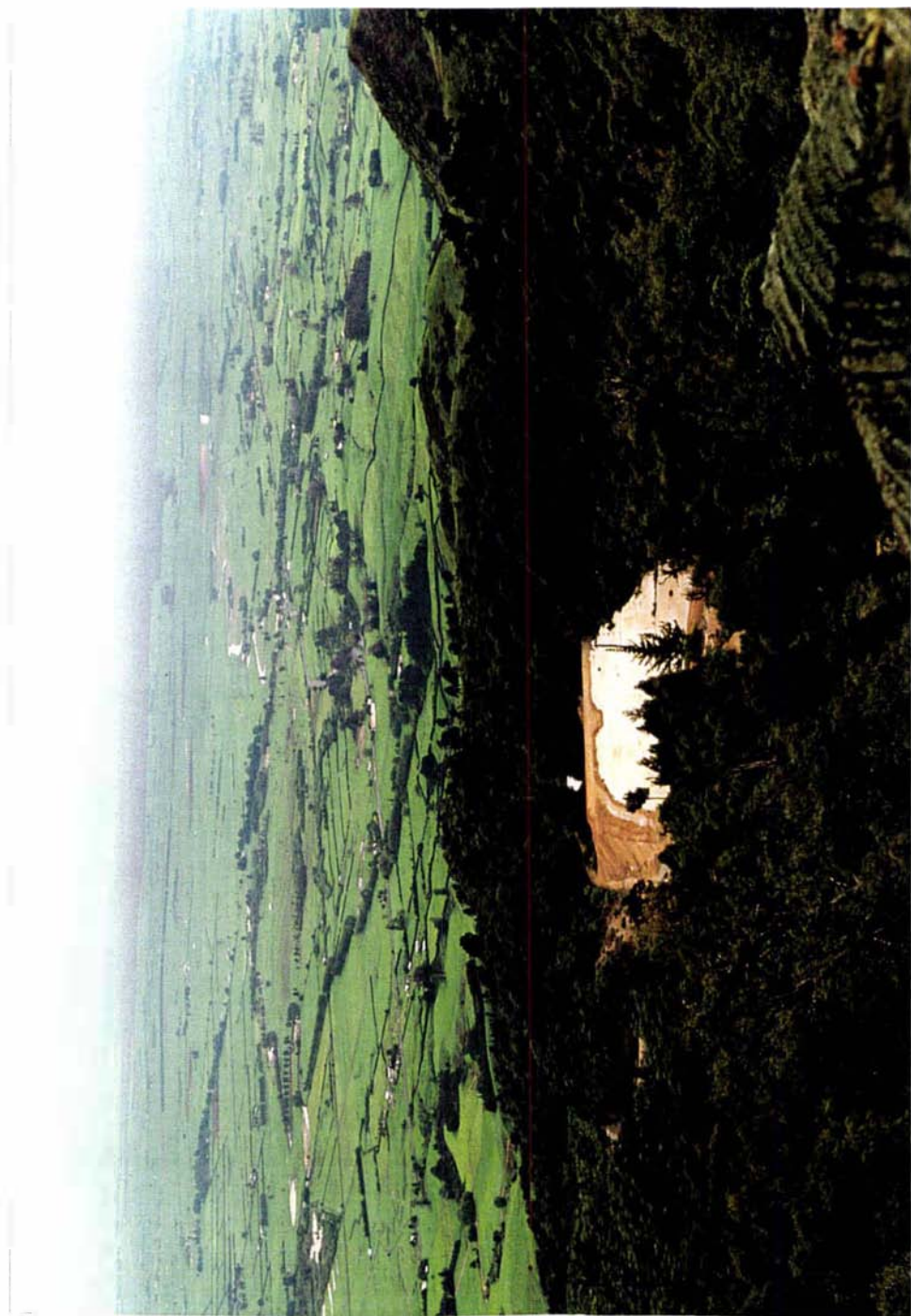


Plate 2.1 Panoramic view of the Tui tailings dam and Hauraki Plains (August 1993).

Hardwood species, including Kamahi (*Weinmannia racemosa*), Rata (*Metrosideros robusta*), Tawa (*Beilschmiedia tawa*) and Tawari (*Ixerba brexioides*) dominate the upper canopy, while smaller trees including Five-finger (*Pseudopanax arboreus*), Hangehange (*Geniostoma rupestre*), Mahoe (*Melicytus ramiflorus*), Mamaku (*Cyathea medullaris*), Pate (*Schefflera digitata*), Pigeonwood (*Hedycarya arborea*) and large-leaved coprosmas make up the under-story. Epiphytic *Astelia* species and climbers such as keke, creeping rata, mangemange and supplejack are also present. The ground cover is dominated by mosses and ferns because of the moist conditions prevailing on the Mountain (Bollard, 1991). At higher altitudes the canopy more commonly consists of Tawari, Tawherowhero (*Quintinia serrata*), Toatoa (*Phyllocladus glaucus*), Kamahi and *Dracophyllum* species, with the podocarps Miro (*Prumnopitys ferruginea*) and Totara (*Podocarpus totara*) as emergents (Salmon, 1980; Bollard, 1991).

Toetoe (*Cortaderia* spp.) is one of the most prevalent plant species found growing on the abandoned roadways and processing areas of the Tui mine site. The site's moist conditions and low fertility suits the growth of most of toetoe species which are often found colonising roadsides and stream banks throughout New Zealand (Pollock, 1986). Small clumps of Toetoe have also established on the tailings dam at sites where decaying vegetation (tree trunks/limbs) has provided a suitable micro-environment for its growth. Small trees and shrubs including Manuka (*Leptospermum scoparium*), Puka (*Griselinia lucida*) and Toro (*Myrsine salicina*) are similarly seen growing in organic debris at a few locations upon the tailings (Plate 2.2).

2.3 Climate

Although there is no specific climatic data for the Tui mine site, reliable meteorological data has been collected at Te Aroha township since 1888 (NZMS, 1983). Te Aroha lies 3 km SW of the Tui mine site at an altitude of 18 m (approximately 330 m below the Tui tailings dam). Mean annual rainfall at the town is 1459 mm and is spread over an average of 135 rain-days each year (NZMS, 1983). Rainfall is distributed relatively evenly throughout the year, although an average of 79 mm more rainfall is received during July than January. Heavy deluges of rain frequently occur throughout the year.



Plate 2.2 The Tui tailings dam and surrounding vegetation. The mine adits are located in dense bush in the top centre and left-hand-side of the photograph. (August 1993).

The mean annual air temperature at Te Aroha is 14.5 °C. Mean monthly temperatures vary from 19.5 °C in January to 9.3 °C in July. Temperature extremes of 35.0 °C and -6.1 °C have been recorded in the months of January and August respectively. The town receives an average of 20 ground frosts and 18 days of heavy winter fogs each year. Occasional snowfalls occur on the upper slopes of Mt. Te Aroha which are subjected to fog on an average of 190 days per annum (Bollard, 1991). Average relative humidity at the township varies from around 74% in January to 86% in May (NZMS, 1983). The prevailing wind in the area is a westerly which at times reaches gale force along the ridges of the Kaimai Ranges.

2.4 Site Hydrology

The impact of mining activity on the ground and surface water quality at the Tui mine site has been well studied over the past two decades. Scientific interest in the quality of the Tui and Tunakohoia Streams stemmed largely from the fact that the streams formed an integral part of Te Aroha's town water supply between 1968 and 1979 (Fyson, 1991). Distinctive iron-staining and colloidal deposits in the Tui Stream can be traced from where the tailings discharge enters the stream through to its confluence with the Waihou river (Tay, 1980). Concentrations of Fe, Mn and Cd in water collected from the former intake screen of the Tui Stream were found to exceed World Health Organisation (WHO) limits for drinking water by 56, 35 and 1.5 times respectively (Tay, 1980; World Health Organisation, 1984a, 1984b). The pH of the water was found to vary 2 to 3.5 pH units below the recommended WHO levels. Although town water is no longer obtained from the Tui and Tunakohoia streams, there is concern that shallow ground water used for domestic water supply in the vicinity of the tailings dam may be contaminated with heavy metals (Pang, 1995).

Several studies have been undertaken at the Tui mine site investigating various aspects of the site's hydrology and the impact of past mining activity on water quality (Tonkin & Taylor, 1974; Ward *et al.*, 1976; Tay, 1980; Pang, 1992). The impact of the Tui mining operation on the aquatic environment was also investigated as a part of two comprehensive studies conducted in the late 1980's by the now defunct 'Water and Soil Directorate' of the Ministry of Works and Development (Smith, 1986; Livingston, 1987). Research indicates that 'background' concentrations of Cd, Cu, Pb and Mn in

ground and stream water in the vicinity of the mine site are naturally elevated due to base-metal mineralisation in the country rock (Pang, 1995). Even water taken from stretches of the Tui Stream not effected by mining and from the south branch of the Tunakohoia stream was found to contain concentrations of Cd and Pb exceeding WHO guidelines for drinking water (Table 2.1).

The effect of Norpac's past mining operation has been to exacerbate the problem of heavy metal contamination of surface and groundwater in the vicinity of the Tui Mine. This is evidenced by the extremely poor quality of water in the north branch of the Tunakohoia (northern Tunakohoia) Stream and in the Tui Stream downstream of its confluence with the tailings stream (Table 2.1, Figure 2.1). The mine adits and the tailings impoundment are the two primary sources of contaminated water in the study area. The surface water draining from the abandoned mine adits is intercepted largely by the northern Tunakohoia Stream. Although drainage from the mine adits is generally alkaline (pH 7.4 to 7.7), the water contains high concentrations of Cd, Mn, Pb and Zn (Pang, 1995). Whilst this mine drainage does not exhibit acidic pH, it has appreciable mineral acidity associated with dissolved metals and is potentially as hazardous as the acidic drainages emanating from the tailings (Chapter 3.4).

Groundwater flow modelling suggests that the northern Tunakohoia Stream may also receive drainage from the tailings dam, however, the majority of this highly contaminated water is believed to flow into the Tui Stream and into the groundwater via fractured andesitic bedrock (Pang, 1992, 1995). Elevated levels of heavy-metals in the northern Tunakohoia Stream has rendered the stream largely devoid of life. Dilution by 'uncontaminated' water of the south branch of the Stream, however, largely mitigates these adverse environmental effects downstream of the confluence (Pang, 1995).

The Tui Stream is substantially more acidic and generally hosts higher concentrations of Fe and Mn and lower concentrations of Cu, Pb and Zn than the northern Tunakohoia Stream (Table 2.1; Livingston, 1987; Pang, 1995). This trend may reflect the predominance of acid generating iron pyrite (FeS_2) in the Tui tailings. Arsenic levels in the Tui Stream were found to be lower than in many other streams contaminated by

Sample Location	pH	As [µg/l]	Cd [mg/l]	Cu [mg/l]	Fe [mg/l]	Mn [mg/l]	Pb [mg/l]	Zn [mg/l]	Reference
Tailings Leachates	2.7 - 4.0 2.6 - 3.2	– –	0.35 - 0.75 0.21 - 0.56	0.84 - 9.15 0.07 - 3.13	737 - 906 118 - 311	98 - 102 26.5 - 39.0	0.80 - 2.68 1.30 - 2.45	224 - 302 70.0 - 113	Tay (1980) Pang (1992)
Tui Stream	4.5 - 5.1 6.7 5.9 - 6.4	– – 1.0 -1.5	0.02 - 0.03 < 0.05 ≤ 0.02	0.04 -0.27 < 0.02 0.04 - 0.23	3.7 -18.3 0.55 –	1.74 0.42 –	– < 0.10 0.02 -0.06	5.1 - 11.0 1.01 2.08 -17.0	Tay (1980) Pang (1992) Livingston (1987)*
Tui Stream (control)	7.1-7.8 6.5	– –	≤ 0.01 < 0.02	≤ 0.03 < 0.01	<0.03 - 0.15 0.10	<0.01 < 0.05	0.02 - 0.50 < 0.10	0.02 0.10	Tay (1980) Pang (1992)
Nth. Tunakohoia	7.4 - 7.7 7.5	– –	0.01 - 0.13 <0.05 - 0.14	0.01 -0.05 <0.02 - 0.11	<0.04 - 0.10 0.20-4.05	<0.01 - 0.74 <0.09 - 1.10	0.04 - <0.10 0.11 - 0.51	1.59 - 16.2 2.30 - 16.0	Tay (1980) Pang (1992)
Sth. Tunakohoia	6.7 - 7.5 6.9	– –	0.01- 0.02 < 0.05	0.01 - <0.03 0.02	0.03 - 0.06 0.10	0.01 - 0.05 < 0.09	<0.03 - <0.10 < 0.10	0.01 - 0.50 < 0.09	Tay (1980) Pang (1992)
WHO Guidelines	6.5 - 8.5	50 [†]	0.005 [†]	1.0*	0.3*	0.1*	0.05 [†]	5.0*	(WHO 1984a/b)

Table 2.1 Typical water quality of the tailings leachates, the Tui Stream both below and above (control) its confluence with the tailings leachates, the northern and southern branches of the Tunakohoia Stream below the mine site and World Health Organisation (WHO) Guideline values for drinking water. * Unfiltered water samples were used in this study. [†] Health guidelines for inorganic constituents. * Aesthetic guidelines for chemical constituents that may affect the quality of drinking water though seldom found in toxic concentrations.

mining activity in the Coromandel region (Livingston, 1987). Research indicates that the high concentrations of metals in the lower reaches of the Tui Stream originate from acid mine drainage (AMD) emanating from the Tui tailings dam (Tay, 1980). An overview of the generation of acid from sulphide oxidation and the formation of contaminated mine drainages and AMD is discussed in Chapter 3 (sections 3.3 & 3.4).

Due to its topographically low position, the tailings dam and pond is thought to be a local discharge area of up-gradient groundwater. Groundwater flow modelling and water level contours suggest that about 200 to 450 m³ of leachates percolate into the groundwater from the tailings dam each day (Pang, 1995). Leachates generated by groundwater saturation of the tailings and by rainfall infiltration collect in a silt trap to form a small pond below the tailings dam (Plate 2.3). The water draining from the pond flows into a small stream containing diverted spring and surface water from the tailings and adjacent land. The resulting stream has approximately a third of the flow of the Tui Stream and intersects the larger stream about 300 m downstream of the tailings dam (Tay, 1980). The inflow of this highly contaminated water into the Tui Stream not only increases the water’s metal content but also substantially elevates the stream’s acidity, sulphate content and total hardness, whilst reducing its alkalinity (Table 2.2).

A large difference between total hardness and alkalinity is often indicative of AMD-impacted streams (Livingston, 1987; Ritcey, 1989). This difference arises due to the consumption of the water’s alkaline anions (eg. carbonate and bicarbonate) by introduced acid. The alkalinity is reduced relative to the total hardness (calcium and magnesium ion content) by an amount equivalent to the quantity of acid neutralised (Livingston, 1987).

Table 2.2 Water quality parameters for the Tui Stream, and background values for six Coromandel streams. (Adapted from Livingston, 1987).

	Total Hardness (g/m ³ CaCO ₃)	Alkalinity (g/m ³ CaCO ₃)	Sulphate (g/m ³ SO ₄)
Tui Stream	69.8	1.1	90.2
Background	16.9	14.6	6.4



Plate 2.3 Silt trap situated below the front (western) face of the Tui tailings dam (August 1993).

Biologically, the Tui Stream is one of the most degraded streams in the Coromandel Region as indicated by the extremely low diversity and numbers of macro-invertebrates in its waters (Livingston, 1987). A survey conducted on the stream in the early 1980's found it to be devoid of fresh water fish (Penny, 1983). Although the survey was able to identify past mining activity as the general causative factor in biological impoverishment of the stream, it was unable to identify the specific factor or factors responsible. It was recognised that it may have resulted from one of several chemically interdependent parameters including toxic metal concentrations, low pH conditions and the deposition of excess fine sediments and/or precipitates. Some correlative evidence did indicate, however, that high metal concentrations in the stream (particularly Zn) may be causing toxicity (Livingston, 1987).

Unless control measures are undertaken to mitigate sulphide oxidation at the Tui mine site, AMD is likely to continue impacting adjacent streams and groundwater in the vicinity of the dam for many hundreds of years. Pang (1995) estimates that more than 16 tonnes of various heavy metals will be released from the tailings into groundwater and streams over next few millennia. The release of such large quantities of metals, including Cd, Cu and Pb into the environment is of great concern due to the potential health risks these metals pose to humans and due to the adverse impact they are currently having and will continue to have on the aquatic system.

2.5 Geology

The Tui Mine is located within the Hauraki Goldfield, a region that hosts some 47 identified epithermal gold-silver and base-metal deposits (Christie & Robinson, 1992). The goldfield is approximately 200 km long and up to 40 km wide, extending from Great Barrier Island in the north down to Te Puke and across to Te Aroha in the south-west (Brathwaite *et al.*, 1987). The region hosts two dominant types of mineralisation, disseminated 'porphyry' type and 'epithermal' vein type (Livingston, 1987). Although both kinds of mineralisation originate from hydrothermal activity, the majority of the economic deposits in the region (including the Tui Mine) are epithermal. This type of mineralisation is characterised by discrete, well-defined deposits that often produce high grade ore. The Tui's Champion vein reportedly yielded about 28 g of gold per ton of ore

(Robinson, 1974), a value typical of the region's epithermal gold deposits that usually yield between 3g and 30g of gold per m³ (Livingston, 1987).

The potential economic importance of the Tui mineral deposits, which lie on the southwestern margin of the Hauraki Goldfield, was realised soon after their discovery in 1884. Henderson & Bartrum (1913) were among the first to publish information relating to the Tui mine site's geology and history. Rising base-metal prices in the early 1960's prompted renewed interest in the area, resulting in the initiation of several studies that investigated the geology and mineralogy of the Tui deposits. Research includes that of Schofield (1967), Cochrane (1969), Weissberg & Wodzicki (1970), Wodzicki & Weissberg (1970), Adams *et al.*, (1974) and Robinson (1974). A useful review of the mine's early history and geology is included in Williams (1965). Research investigating the geology and mineralisation of the wider region includes that of Boyle (1979), Hochstein & Nixon, (1979), Brathwaite *et al.*, (1987), and Christie & Robinson, (1992). Brathwaite & Christie (1996) have recently completed a geological report and map of the Waihi area which summarise the region's stratigraphy, geological structure and economic geology.

2.5.1 Tectonic Setting

The igneous rocks of the Hauraki region were produced during the Miocene and Pleistocene by intrusive and volcanic activity occurring in a NNW trending continental margin arc. This arc is believed to have been associated with a westward dipping subduction zone that once existed east of the Coromandel peninsula (Skinner, 1986). Cole & Lewis (1981) suggest that the Hauraki arc may have evolved into the presently active Taupo-Hikurangi subduction system. The main phase of andesitic volcanism in the Coromandel Peninsula is thought to have occurred between 10 and 15 m.y. ago (Livingston, 1987), contemporaneously with the intrusion of high level porphyry plutons and with minor eruptive activity at the southern end of the Northland Peninsula (Cole & Lewis, 1981). The change to rhyolitic volcanism that took place approximately 6 m.y. ago in the Hauraki Volcanic Region is apparently related to tensional faulting in a marginal basin (Cole & Lewis, 1981).

2.5.2 Regional Setting

The Hauraki Goldfield coincides with a continental margin volcanic zone (Coromandel Volcanic Zone) that consists of thin alternating beds of complexly folded Mesozoic greywackes and argillite, unconformably overlain by Miocene to early Quaternary sub-aerial, andesite-dacite-rhyolite volcanics and volcanoclastics (Brathwaite *et al.*, 1987). Jurassic greywacke and argillites constitute the basement rocks of the whole region and have been folded approximately along the axis of the peninsula (Robinson, 1974). Extensive block faulting is evident in the form of normal faults within the basement rocks along NW to NNW and NE, ENE trends that gives rise to horst and graben structures (Brathwaite *et al.*, 1987). The whole region has been tilted to the SE, exposing the Jurassic basement rocks in areas north of Thames (Hochstein & Nixon, 1979).

The overlying volcanic rocks, which range in composition from andesites to rhyolites with rare basalts, become progressively thicker and younger to the south where they merge with the Quaternary volcanic deposits of the Taupo Volcanic Zone (Wodzicki & Weissberg, 1970). In order of decreasing age the more important volcanic units of the Hauraki Goldfield include; the Beesons Island Volcanics (dominantly andesitic Miocene rocks, c.16 m.y.); the Whitianga Group and Minden Rhyolite (rhyolitic rocks of Pliocene age, c. 3-5 m.y.) and the Late Pliocene Omaha Andesites (Adams *et al.*, 1974). Although regional propylitic² alteration of all rock types is ubiquitous, mineralisation in the Hauraki Goldfield is confined largely to the propylitised andesites of the Beesons Island Volcanics (Robinson, 1974). Far fewer vein deposits are found within the hydrothermally altered basement rocks and rhyolitic rocks of Pliocene age and mineralisation is absent in the Omaha Andesites (Adams *et al.*, 1974).

Immediately to the east of the Kaimai and Coromandel Ranges lies the Hauraki Depression which is a large tectonic feature about 20-30 km wide and at least 220 km long. The Depression is bounded on the western and southern sides by the Hunua and Hapuakohe Ranges respectively. Within the Hauraki Depression the basement

² Propylitic alteration refers to weak and often pervasive alteration of rocks caused by hot meteoric waters. It is characterised by a slight reduction in rock strength and by the development of secondary minerals such as chlorite, calcite and pyrite.

Greywacke rocks that form the surrounding ranges are overlain by Quaternary and Tertiary sediments with a combined thickness of up to 3 km (Hochstein & Nixon, 1979).

Based on the striking similarities of the Hauraki Depression to other well studied continental rifts, Hochstein & Nixon (1979) postulate that the southern part of the Hauraki Depression is an active rift formed after the collision of the Indian and Pacific Plates. Active faulting and shallow earthquake activity in the Southern part of the Depression support this theory.

2.5.3 Local Geological Setting

The Tui Mine occurs in extensively hydrothermally-altered volcanic rocks. The most common rock type is massive andesite, although in places the lodes also dissect andesitic breccia and tuffaceous lithologies (Cochrane, 1969; Wodzicki & Weissberg, 1970). K-Ar dating indicates that the andesitic host rocks are of Miocene age and were erupted approximately 16.2 m.y. ago (Adams *et al.*, 1974). Schofield (1967) mapped the country rocks of the Tui Mine collectively as the Te Aroha andesites, a sub-unit of the Beesons Island Volcanics (Schofield, 1967; Robinson, 1974). In locations where the andesite is relatively unaltered the rock consists of phenocrysts of plagioclase, augite and hypersthene in a fine-grained crystalline ground mass with a pilotaxitic texture. The ground mass contains moderate quantities of microscopic quartz (Wodzicki & Weissberg, 1970).

The andesite is overlain by a 3m bed of fine-grained, moderately well layered tuff that has been so strongly hydrothermally altered that no primary minerals remain. Overlying the tuff is an 8 m bed of rhyolitic or dacitic ignimbrite. This deposit contains numerous fragments of argillite, volcanic rocks and flattened pumice, and again is highly altered (Wodzicki & Weissberg, 1970). Above the ignimbrite lies a quartz-bearing volcanic rock, thought to be a dacite or quartz andesite. To the south of the Ruakaka lode, a strongly altered quartz-bearing volcanic breccia probably of dacitic or quartz andesite origin, mantles the underlying units (Wodzicki & Weissberg, 1970).

2.6 Mineralogy of the Tui Ore

The Tui Mine deposits are typical of the epithermal base-metal ore deposits that occur as lodes in fissures and faults in hydrothermally altered Tertiary andesitic and pyroclastic rocks (Boyle, 1979). The Tui Mine consists of two major mineralised quartz reefs (the Champion and Ruakaka) which are up to 2 m and 8 m in width respectively (Robinson, 1974). The reefs intersect in the upper levels of the mine but diverge at depth due to them dipping steeply in opposite directions. The average strike and dip of the Ruakaka and Champion reefs are N 80° E, 68° S and N 40° E, 64° NW respectively (Wodzicki & Weissberg, 1970). Surface outcropping of the reefs is extensive with the strikes of both reefs mapped for distances of over 500 m (Williams, 1965).

The reefs comprise a quartz-cemented wall-rock breccia containing a discontinuous zone of brecciated quartz cemented by sulphide minerals and a younger generation of quartz (Robinson, 1974). The minerals constituting these lodes were deposited in fault controlled, open space filling type environments in which fissures formed and remained open for sufficient lengths of time to enable the formation of coarse-grained sulphide minerals (Wodzicki & Weissberg, 1970). The ore at the Tui Mine is thus characterised by lenticular masses of sulphide minerals that are interspersed between barren portions of quartz and remnant andesite breccia (Robinson, 1974). The ore (defined as sulphide mineralisation with total Cu + Pb + Zn greater than 5%) is generally coarse-grained, with 3 cm crystals of sphalerite and galena being common (Wodzicki & Weissberg, 1970).

The sulphide rich zone that forms the ore bodies varies in thickness from approximately 0.05 m to exceptionally greater than 0.9 m and has an average width in the vicinity of 0.5 m (Cochrane, 1969). The ore body in the Ruakaka lode is generally wider and more continuous than that of the Champion lode. Wodzicki & Weissberg (1970) suggest that this may be due to the Ruakaka lode's stronger normal faulting component and generally steeper dip. These factors are thought to have influenced the size and persistence of the fissures that were ultimately filled with epigenetic mineralisation (Wodzicki & Weissberg, 1970).

The Tui ore is essentially an aggregate of sphalerite (ZnS), galena (PbS), chalcopyrite (CuFeS_2) and pyrite (FeS_2) with subordinate marcasite (FeS_2), and tennantite ($(\text{Cu, Fe})_{12}\text{As}_4\text{S}_{13}$) in quartz gangue (Williams, 1965). Appreciable amounts of tetrahedrite ($(\text{Cu, Fe})_{12}\text{Sb}_4\text{S}_{13}$) and trace quantities of cinnabar (HgS) also occur in the ore (Wodzicki & Weissberg, 1970). Late stage alteration minerals include chalcocite (Cu_2S), covellite (CuS), anglesite (PbSO_4) and cerussite (PbCO_3), but these generally occur in minor quantities only (Cochrane, 1969). Sphalerite is the most abundant of the sulphide minerals in the deposits followed by galena, chalcopyrite and pyrite. Although pyrite is not the most abundant sulphide, unlike the other sulphide minerals that are restricted to the lodes, pyrite is also found widely disseminated in the altered wall-rocks (Wodzicki & Weissberg, 1970). The ore yielded an approximate grade of 16.7% zinc, 7.0% lead and 0.62% copper in addition to significant quantities of gold and silver (Wodzicki & Weissberg, 1970).

Quartz (SiO_2) is by far the most abundant gangue mineral in the lodes, however, well crystallised kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is also common throughout the ore body. Carbonate minerals are a minor component of the ore with only small quantities of calcite (CaCO_3) and siderite (FeCO_3) present (Cochrane, 1969). In all, over 70 species of minerals have been identified in the ore and host rocks of the Tui Mine, making it one of New Zealand's "*most prolific mineral localities*" (Courtney *et al.*, 1990).

Despite considerable variations in metal ratios within the different lodes, Wodzicki & Weissberg (1970) noted that textural relations between the minerals were remarkably constant, with both vein systems exhibiting the same minerals and paragenetic sequences. Mineralisation is believed to have occurred during two distinct phases. The first phase resulted in the formation of barren quartz veins varying in thickness from about 1.5 to 5 m. These quartz veins were deposited along previously active fault planes and contained numerous angular shaped, highly altered wall rock inclusions. Renewed movement along the fault planes caused brecciation of the quartz and the rock wall inclusions, forming a porous zone containing numerous cavities. It was within this zone that the minerals of the second phase of mineralisation were deposited to ultimately form the Champion and Ruakaka lodes. Included in the minerals are galena, sphalerite,

tennantite and cinnabar as well as at least two generations of quartz, pyrite and chalcopyrite (Wodzicki & Weissberg, 1970).

2.6.1 Origin of Sulphide Mineralisation

Research indicates that the zoned alteration pattern in Tui Mine's host rocks is genetically related to ore emplacement, as evidenced by the increasing concentrations of As, Cu, Hg, Pb, Sb and Zn in the country rock with increasing proximity to the lode (Weissberg & Wodzicki, 1970). It is believed that the ore metals were added to the lodes and wall rocks by hydrothermal solutions ascending along the initially porous brecciated zones within the quartz veins (Cochrane, 1969; Weissberg & Wodzicki, 1970).

K-Ar dating of the hydrothermally altered andesites associated with ore formation indicates that mineralisation occurred at least 2.6 m.y. but less than 7.0 m.y. ago, contemporaneously with the Pliocene volcanism of the region. Adams *et al.*, (1974) suggest that the alteration most probably occurred between 2.6 and 4.0 m.y. ago, with the date of 7.0 m.y. being erroneously high due to the introduction of excess radiogenic argon during alteration.

The Tui ore's relatively high base-metal sulphide content (>10%) is believed to result from its deposition in a slightly deeper and higher temperature environment than usual (Brathwaite *et al.*, 1987). Sulphur isotope studies indicate that the major sulphide minerals were deposited at temperatures of between 250 and 400 °C (Robinson, 1974; Christie & Robinson, 1992). The exact origin of the mineralised solutions is not known. Cochrane (1969) suggests that they may be related to the loss of volatiles during the late stages of solidification of a plutonic stock below Mt. Te Aroha. Similarly Weissberg & Wodzicki (1970) suggest that the ore metals may have originated from some deep seated magmatic process, or alternatively from trace-metal depleted volcanic rock or basement greywacke at depth. Based on isotope data, Robinson (1974) suggests that the Pb in the deposits originated from basement greywackes. There are two schools of thought as to the origin of sulphur in the deposits. Christie & Robinson (1992) believe that the sulphur was derived from Tertiary volcanic magmas with slight crustal contamination, however this contrasts with previous interpretations that postulated that the sulphur was

hydrothermally leached from greywacke basement rocks (Robinson, 1974; Robinson & Christie, 1980).

These differing theories suggest that the origin of the hydrothermal solutions is complex. The water, trace elements, sulphur and ore metals forming the mineralised solutions may each have originated from a different source. The deposits of the Tui Mine may well represent an ancient geothermal system similar to the deeper parts of those presently active in the Taupo Volcanic Zone (Weissberg & Wodzicki, 1970; Brathwaite & Blattner, 1995).

2.7 Soils

According to the New Zealand Genetic soil classification system the soils in the area of the Tui mine site are classified as *Steepland soils related to brown granular clays* (Taylor & Pohlen, 1962; Wilson, 1980). The soils belong to the Aroha steep land soil series and have formed under mull-forming dicotylous-podocarp forest. Near Te Aroha, the soils have developed on weakly argillised and propylised andesitic parent material at relatively high altitudes (120 m - 750 m) and under high rainfall (c.2000 mm/yr). Whilst the soil depth varies considerably with the steepness of the terrain, the soils typically consist of shallow forest litter (3 cm) and shallow topsoil (15 cm) horizons overlying 30 cm of subsoil. The topsoils are usually dark brown in colour and exhibit clay loam texture and moderately to weakly developed medium nut and crumb structure. The subsoils typically exhibit clay loam to sandy clay loam textures and weakly developed medium blocky and nut structures. The soils are generally well to excessively drained and have low nutrient status (Wilson, 1980). Their greatest limitations are their low nutrient status, steep slope and associated severe erosion risk. They are poorly suited to pastures and are generally used for timber production or catchment protection under native or exotic forest (Gibbs, 1980; Wilson, 1980).

Under the recently developed New Zealand Soil Classification the soils developed upon relatively stable sites, with deeper profiles and strongly developed granular structures, would probably be classified as *Acidic Orthic Granular Soils*, whilst the shallower soils (profiles depth < 75 cm) that have developed on steeper slopes, probably equate to *Acidic Orthic Brown Soils* (Hewitt, 1993).

2.8 The History of mining at Te Aroha

Mining has played an important role in New Zealand's development as a nation, as it not only provided valuable overseas revenue during the initial phases of European colonisation, but also helped to establish the pattern of settlement in New Zealand (Williams, 1985). The township of Te Aroha is one of many such settlements which sprang into existence largely as a result of mining activity in the Coromandel.

Reports of gold in the Te Aroha region date back as far as **1838**, when George White of Whitianga reportedly discovered auriferous ore in the ranges 'opposite' Te Aroha. It is believed that White was referring to the Hangawera Ranges. It was not until **1879**, however, that any 'substantial' discovery of ore was to be made. A prospector by the name of Hone Werahiko found a small 'rich' reef in a gully, immediately to the left of Bald Spur. The ore-bearing reef was found "*just behind the present township, at a height of nearly 1000 ft [305m] above-sea-level*" (Henderson & Bartrum, 1913). This discovery led to a gold rush to the locality but the district was virtually deserted within 6 months, as no workable claims were established (Downey, 1935).

The most promising of the Te Aroha deposits was the Champion lode discovered by A. C. Cornes in **1884**. The lode lay in "*inaccessible country near the Tui creek on the Karangahake range*" (Salmon, 1963). The Champion Mine was set up at the site and after several name changes, this mine was to eventually become known as the Tui Mine. The lode was rich in Pb, and was originally mined with the intentions of supplying Pb flux for smelting gold ore from the Waiorongomai Valley, approximately 7 km to the west.

In the early **1880's**, about 30 companies were formed on the Waiorongomai Valley goldfield and a large battery was built on the flats, at the entrance of the Valley, to crush ore from the different claims (Galvin, 1906). The battery was commissioned by Messrs. Firth and Clark, and was described as being "*one of the finest stamping-batteries in the colony*" (Henderson & Bartrum, 1913). To enable the various claim-owners to supply ore to the plant, the Piako County Council constructed a 3 mile tramway at a cost of £19,000. In **1888** a £20,000 concentrating and smelting plant was erected. This plant was widely regarded as the "*most up to date reduction works in the Australian*

Colonies” (Henderson & Bartrum, 1913). Approximately one ton of Pb flux was required for every ton of Waiorongomai ore concentrate smelted and much of the substantial investment made in Waiorongomai Valley was based on the assumption that the Tui Mine could supply sufficient Pb for this purpose (Downey, 1935). Unfortunately it was soon discovered that the Tui ore contained as much Zn as it did Pb, rendering it “*quite unsuitable*” for use as a flux (Downey, 1935). The whole mining operation in the Waiorongomai Valley was described by Downey (1935) as being “*one long chapter of disaster for the many companies that ventured their capital into it.*” The main reason for the large financial losses were due to the fact that many of the owners “*had not taken the precaution to see that the underground appearances of the mine warranted the outlay*” (Downey 1935). Although initial assays of the Tui and Waiorongomai ore proved highly satisfactory, the ore whilst valuable “*was so complex that by the recognised method of treatment - crushing and amalgamation - very little of its valuable contents could be recovered*” (Galvin, 1906).

The refractory nature of the Tui ore did not deter mine development and by **1889** three adit levels had been constructed and communication made between them on the main lode. An aerial tramway was under construction to take the ore 120 chain ($\cong$ 2.5 km) down the mountain to the flats below (Carter & Pharo, 1965). The earliest known owners of the Tui Mine were the ‘Thames Lead and Silver Company’, the mine, however, changed ownership many times during its early days.

When it was realised that the Tui ore was unsuitable as a source of Pb for the smelters, attention turned to the mine as a potential source of the noble metals, gold and silver. In **1888** 11 tons of Tui ore were sent to England realising £ 6 10s per ton. This was intended to be the first batch of some 200 tons of ore bound for England, however, no further ore was sent due to the poor yields of bullion being recovered from the ore (Downey, 1935).

By **1893** the Company operating the mine was facing financial difficulty, because they were still unable to find an economical means of processing the ore. As the Waiorongomai smelter had only managed to extract approximately 30% of the bullion from the Tui ore, so it was decided to wait for work to be completed on a new

processing plant, based on the more economical ‘cyanogen process’. This process proved unsuccessful due to the Tui ore’s high chalcopyrite content which resulted in the excessive consumption of cyanide (Galvin 1906). In **1896** the New Zealand Syndicate bought the lease and then in **1897** the mine changed hands once again with the Tui Gold-Mining Company acquiring the lease. By this stage five adit levels had been opened on, or near, the Champion lode and had been driven in for distances between 9 and 83 m (Downey 1935). The Tui Gold-Mining Company apparently undertook little work to further develop the mine.

In **1899** a further attempt to process the ore, using the thermo-hyperphoric method³ developed by the Rev. Joseph Campbell, also failed to economically extract the precious metals (Henderson & Bartrum, 1913). When this process failed, the claim was abandoned until **1902** when a local syndicate took up the lease. The mine changed ownership several times after **1902**, but little work was to be carried out until about **1960**, when interest was once again sparked in the Tui Mine by steadily rising base-metal prices.

The potential of the Tui Mine as a source of Cu, Pb and Zn, rather than as a source of gold and silver was mentioned by Baker in **1930** (Hodder & Scadden, 1981) but it would be more than 30 years until the mine would reopen. In **1962** South Pacific Mines Ltd. acquired the lease to prospect and evaluate the area as a base-metal proposition. They subsequently reopened the lower 3 levels of the old workings and prospected the lodes using ‘horizontal drives’. In **1966** Norpac Mining Ltd. was formed as a subsidiary of the Cable Price Downer Group, acquiring the assets of South Pacific Mines Ltd. (Cochrane, 1969). In the same year Norpac was granted two mining licenses and developmental work was started on the mine, including the driving of a new low level cross-cut to provide access to the Champion and Ruakaka reefs (Bollard, 1991).

By the end of **1967** Norpac Mining Ltd. had opened a number of stopes to supply ore to a mill and flotation plant that was built adjacent to the then proposed tailings dam. The

³ The thermo-hyperphoric method refers to a process where the ore was heated to a temperature of 1200 °F in the presence of water gas to create a free-milling ore (Henderson & Bartrum, 1913).

destination of the ore concentrate was the Mitsui Mining and Smelting Company of Japan. The ore concentrate was shipped out of New Zealand via the Port of Tauranga. Mining at Tui was undertaken by ‘shrinkage stoping’, a method of underground mining where the roof of the mine is selectively caved in and used to work on as a floor, allowing progress to be made along the lode (Hodder & Scadden, 1981). By January **1969** ore was being extracted and processed at the Tui Mine at the rate of 100 tons/day. After processing, 100 tons of ore would yield about 10 tons of concentrate, with a market value at the time of approximately \$200(NZ) /ton (Cochrane, 1969).

During its heyday the mine employed 64 people and pumped some \$250,000 in salaries into the local economy, annually. In addition to the Pb-Cu-Zn concentrate produced each year, small quantities of Cd, Ag and Au were also produced (McGrath, 1973). A total of 163,000 tonnes of ore was extracted from the Champion and Ruakaka reefs, yielding 13,159 tonnes of Zn concentrate, 7,755 tonnes of copper/lead concentrate, 2,220 oz (63 kg) of gold and 98,000 oz (2778 kg) of silver (Bollard, 1991). There is some variation between production figures among different sources (McOnie, 1987; Bates, 1989).

In **1971** mining operations were marred by the slumping of several thousand tonnes of mine waste into an adjacent stream following a rainstorm in which approximately 230 mm of rain fell in 24 hours (Fyson, 1991).

After several years of ‘successful’ operation, falling Cu prices and growing environmental concerns about alleged high mercury levels in the Tui ore, prompted the Mitsui company of Japan to relinquish their contract when it expired in **1972** (McGrath, 1973). The last shipment of ore concentrate (3000 tons) was exported to Japan in July **1973**, after which time the ore was stock piled while new customers were desperately sought. Despite **1970** estimates indicating that some 250,000 tonnes of ore remained (sufficient to keep the mill operational until **1978**) and grants totaling \$418,000 were made available to help establish new buyers, none were found. By November **1973** only 14 people remained on the payroll and a receiver/manager was appointed for the Norpac Company (McGrath, 1973). Finally in **1974** New Zealand’s only base-metal mine closed and all of its assets were sold. During its operation the mine accounted for 80% of all

New Zealand's mineral exports and earned a total of \$4 million in foreign exchange (McGrath, 1973).

Mineral Resources (NZ) Limited purchased some of Norpac's assets from the receiver in 1974. These included the Tui plant and mining licenses, however, exploration was not resumed in the area until 1983. A base metal and gold prospecting program was initiated that included "*gridding, soil sampling, geological mapping and channel sampling...*" (Bollard, 1991). In 1987 Mineral Resources subsidiary, Tasman Gold Development Limited, applied for a prospecting license for a 196 Ha site on the Northern slopes of Mt. Te Aroha, an area which included the old Tui Mine (the Tui Tailings Dam lay immediately to the east of the application area). Tasman Gold's primary mining interest in the site was as a source of gold, however it also intended to continue the evaluation of the area as a potential source of Ag, Cu, Pb and Zn.

More than 30 official objections were lodged against Tasman Gold's application. The major points of concern raised by the objectors related to the detrimental effects on the environment caused by Norpac's past activities and that further mining activity in the area would cause even more damage, primarily due to the presence of sulphides in the ore (Bollard, 1991). Another major area of concern was the steep topography and land instability, especially when adverse weather conditions prevailed. Other objections were based on the ecological, historical and cultural value of the land, with particular reference to past Maori occupation (Bollard, 1991).

In an "historic" ruling in July 1991 the Planning Tribunal quashed the intentions of the Mining Company by turning down its application. Upon deliberation of its verdict the Tribunal admitted, that based upon the evidence submitted during the hearing, carefully controlled prospecting "*...would not be likely to have any major additional impact on the environment, nor place the Te Aroha town water supply...at risk*" (Bollard, 1991). The Tribunal, however, also held the view that "*a commercially feasible mining operation would not be possible without grave risk of further unacceptable environmental impact*". Since the prospecting was precursory to mining, the Tribunal rejected the application because they believed that the environmental risk was

unacceptable, a risk it saw against an historical background of “*a most regrettable, albeit instructive, legacy of environmental degradation*”.

The decision was based on the AMOCO Minerals case in 1982 where it was ruled that “*it may be that the environmental importance of certain land is so high that it can be said immediately that, whatever the value of the mineral deposits in it might be, the land should never be disturbed by mining operations and that therefore not even a prospecting license should be issued*” (Bollard, 1991). In its ruling the Tribunal noted among other things; (1) the steepness of the area, (2) the potential for storm-induced debris movement, land slips and erosion, and (3) the potential risk of heavy metal contamination to Braeside Aquaria’s water supply (Orsman, 1991). Tasman Gold Development Ltd. had spent \$802,000 in preliminary prospecting of the area prior to the Tribunal’s ruling (Bollard, 1991). An appeal was subsequently lodged against the Tribunal’s decision by the applicant, however, it was overruled and to date no further prospecting has taken place on Mt. Te Aroha.

2.9 Tui Mine Politics

The Matamata-Piako District Council and the Department of Conservation (DOC) are currently the “*reluctant*” owners of the land upon which the tailings dam lies (WRCM, 1991). Any responsibility for the problems associated with the abandoned mine appears to rest with the land owners despite the fact that all revenues derived from the royalties went to the owner of the resource at that time, the Crown (Fyson, 1991). Although most governments have vindicated themselves from any kind of responsibility for cleaning up the Tui mine site, in **1981** the National Government conceded somewhat by making an *ex gratia* payment of \$25,000 to the Hauraki Catchment Board and \$2,500 to the Te Aroha Golf club due to damages arising from the Tui tailings (New Zealand Herald, 1981). At the time many people believed the Government was trying to buy its way out of a “*political storm*” (Wallace, 1981).

The reluctance of the Crown to take responsibility for reclaiming the Tui mine site stems largely from the liberal legislation that existed when the mine was operational. The Tui mining operation was established under the rules of the ‘Wardens Court’, a system that in the mid 1960’s saw its role mainly to promote mining. The Wardens

Court system predated the Water and Soil Conservation Act of 1967 and the Mining Act of 1971, two acts which may have helped to prevent the environmental degradation that was to mar the operation. The one relevant piece of legislature that should have worked to protect the environment seems to have been totally ignored by Norpac (Fyson, 1991). This was the Te Aroha Borough Water Supply Empowering Act of 1962. This Act stated that *“no mining privileges shall be granted over, and no mine waste shall be discharged into the water supply streams or their tributaries”* (Fyson, 1991). At the hearings preceding the initiation of mining, the Hauraki Catchment Board made submissions and objected to the inadequacy of environmental controls being implemented by the mining company. Its views were overruled due primarily to the support the operation had from both the local community and the Government (Hansen, 1989).

The aforementioned acts have all been superseded by the Resource Management Act (RMA) and Crown Minerals Act (CMA) which were both enacted in 1991. The RMA has essentially tightened environmental laws on mining activity, laws that some considered to be already overzealous. Palmer (1982) for example, expressed the view that.... *“Considered as a land use, mining is given a prominence which it probably doesn’t deserve, and the applicants for mining licences are subjected to more vigorous procedures generally than other persons utilising land or resources”*.

Despite what some may consider to be tortuous legislation it is evident that the RMA will ensure that environmental degradation on a scale such as that seen at Te Aroha does not reoccur in New Zealand. The RMA has a new focus on the stewardship of the Country’s physical and natural resources and is designed in part to safeguard *“the life supporting capacity of air, water, soils and ecosystems”* (RMA, section 5(2)b). Therefore activities such as mining which may conflict with the RMA’s objectives must now comply with much more stringent environmental controls. Safeguards have also been set up in the CMA to protect the environment and the rights of the landowners from the potentially adverse effects of mining associated activities.

Recently the Tui mine site has been at the centre of renewed interest, as regional and local authorities and mining companies have been considering options for reclaiming

the site. A background paper was prepared by the Waikato Regional Council in 1991 which briefly discussed the history of the mine, responsibility for the site and possible remedial options (WRCM, 1991). The Waikato Regional Council is currently setting up a technical group to look at cleaning up the Tui mine site. The technical group is likely to include representatives from the Matamata-Piako District Council and Department of Conservation (the joint landowners), the Waikato Regional Council, New Zealand's Mineral Industry, the Ministry of Commerce, the Te Aroha Mining Information Group and Tangata Whenua. The group's main task will be to develop terms of reference and to explore options for the environmental stabilisation of the Tui Mine and process site (EWM, 1995). Much of the impetus for the setting up of the working group has arisen from the interest that Waihi's two currently operational gold mining companies (Coeur Gold NZ Ltd. and Waihi Gold Mining Company Ltd.) have shown in helping reclaim the site (Waihi Gazette, 1995). These companies are undoubtedly keen to see the site rehabilitated as the continued bad press that the Tui Mine generates sheds 'contaminated' light on current mining operations within the region.

3.0 Chapter 2 Summary & Conclusions

- Based on information presented in this Chapter it is clear that the Tui mine site is located within a unique and, in many respects, fragile environment. The surrounding terrain is steep and rainfall at the site is high and frequently intense.
- The land and bush encompassing the Tui mine site forms an important wildlife and recreational area and is rapidly regenerating into an important tract of native forest.
- The Tui mine tailings not only aesthetically mar the landscape but also form a source of highly contaminated water which continues to degrade stream, surface and ground water in the vicinity of the dam.
- The Tui Mine has had a long and 'turbulent' history which appears set to continue until steps are taken to reclaim the site. Whilst responsibility for the reclamation of the Tui mine site currently lies with the Department of Conservation and the Matamata-Piako District Council (who own the site), many believe that the Crown should front the cost of a comprehensive reclamation program, as they set the conditions under which the mine operated and were the original recipients of royalties during the Tui Mine's operational years.

CHAPTER 3

The Reclamation of Mine Wastes

3.0 Introduction

This chapter reviews the problems and practices of land reclamation paying particular attention to the reclamation of sulphide-bearing metalliferous tailings and waste rocks. A cursory review of the reclamation of waste materials generated at aggregate, alluvial gold, coal and titanomagnetite (ironsand) mine sites is also given, however, as it is recognised that many of the reclamation techniques used to reclaim such materials are potentially useful for the rehabilitation of sulphide-bearing materials.

The process of sulphide oxidation and its role in generation of metal contaminated mine drainage and Acid Mine Drainage (AMD) are reviewed, as is the means of predicting and controlling the Acid Generating Potential (AGP) of mine wastes. Particular reference is also given to lime (CaCO_3), composted sewage sludge and metal-tolerant plant species in terms of their ability to aid in the revegetation of sulphide-bearing mine wastes.

3.1 Definitions

In this thesis the terms *reclamation* and *rehabilitation* have been used interchangeably. It is recognised, however, that some researchers distinguish between the terms. McQueen (1982) for example, uses *rehabilitation* to describe the establishment of conditions for a 'new' specified, often productive land use which is substantially different from the original land use (eg. native forest → mine site → pasture), whilst he uses *reclamation* to describe the restoration of derelict land to a use and vegetative state similar to that existing prior to land dereliction (eg. pasture → mine site → pasture).

In the context of this thesis *revegetation* is used to describe a specific form of reclamation which aims at establishing a vegetative cover on land that may or may not have been previously vegetated. The term *restoration*, which is commonly encountered in literature, refers to returning land to its previous topography and vegetation cover. This type of reclamation is often impractical and/or prohibitively costly (Fricker, 1986).

The term *tailings* is mostly used in this study to describe geological materials that have been finely crushed (<2.0 mm) and from which metallic compounds have been extracted for the purposes of refining. In this review no attempt has been made, however, to differentiate between milled tailings and tailings derived from dredging operations which are not intentionally crushed during processing and can range in size from clay and silt-sized particles to boulders (>256 mm).

3.2 Mine Site Degradation & Reclamation

Environmental degradation resulting from both active and abandoned mine sites is a serious problem in many regions throughout the world (Bradshaw & Chadwick, 1980; Sengupta, 1993). Although some degradation is obviously anticipated with an industry which is responsible for the mining and processing of an estimated 24 billion tonnes of minerals each year, many of the problems associated with degraded mine sites are the result of liberal laws which in the past placed few environmental controls on mining practices (Miller, 1992). Continuing environmental damage arising from polluted waters and dispersal of contaminated solid wastes is a common feature of many abandoned mines in North America, Europe, Australia and numerous other countries including New Zealand (Ritcey, 1989; Johnson *et al.*, 1994).

In the US alone, 557,650 hard rock mines have been catalogued and the clean up of these mine sites is expected to cost between \$32 and \$71.5 billion dollars (IALR Newsletter, 1993). Reclamation of one of the most degraded sites (the Summitville Goldmine in Colorado) is expected to cost over \$100 million US dollars alone (Skow, 1993). The clean up of this site will involve the neutralisation and relocation of 6½ million tonnes of acid generating waste to prevent further contamination of the local river system by cyanide and metal contaminated water. Mine site reclamation programs of even greater magnitude are currently being conducted in Germany in the Saxon Erzgebirge region. Uranium mining conducted between 1946 and 1989 has seriously degraded the environment and clean up of the region is expected to take more than 10 years and to cost between 10 and 15 billion German marks (Keller, 1993).

Metalliferous wastes, consisting of mineralised ore materials brought to the surface during mining activities and containing elevated concentrations of one or more heavy metal elements, are notoriously difficult to reclaim (Williamson & Johnson, 1981). The majority of highly contaminated mine sites contain such material and many are plagued with problems specifically associated with the oxidation of remnant sulphide minerals in mine tailings and waste rocks.

3.2.1 Australian Mine Sites

Examples of severe environmental degradation resulting from metalliferous mining operations are not confined to the Northern Hemisphere. Degraded mine sites are found in several Pacific Island countries including, Papua New Guinea (PNG), Solomon Islands, New Caledonia and Fiji (Harris, 1997). PNG is the most heavily impacted of these countries and hosts the well known Bougainville and Ok Tedi copper mines. Some of the most severe environmental degradation in PNG has arisen from the use of rivers as disposal systems for tailings and contaminated mine water.

In Australia, the Broken Hill and Captains Flat mine sites in New South Wales and the Mount Isa and Rum Jungle mine sites in Queensland and the Northern Territory respectively, are classic examples of degraded mine sites. A brief overview of the environmental degradation and reclamation measures that has or is being employed at these 4 sites is given below.

3.2.1.1 Rum Jungle, Northern Territory

Prior to reclamation the Rum Jungle mine site, situated 64 kilometres south of Darwin, was one of the most degraded mining sites in Australia (Bell *et al.*, 1989). Between 1983 and 1986 an estimated \$A18.6 million dollars was spent rehabilitating an experimental heap leach pile, a 32 ha tailings dam, 3 waste dumps and 4 million m³ of highly contaminated water (Bennett *et al.*, 1987; Lowson *et al.*, 1987; Bell *et al.* 1989). Rum Jungle was mined for Cu and U²³⁸ during the peak of the cold war (1954 - 1964) and was finally abandoned in 1971. At that time in Australia little or no legislation existed requiring the reclamation of mine sites, thus many mine sites were effectively left to the elements at the end of mining operations (Bastias, 1987; Ryan, 1987).

The majority of environmental problems that arose at Rum Jungle were related to the presence and oxidation of pyritic minerals within the heap leach pile and waste rock dumps (Harries & Ritchie, 1987). Acid mine drainage emanating from these sulphide-bearing materials seriously contaminated the eastern branch of the Finnis River with acid and a variety of metals including Al, Cu, Co, Fe, Mn and Zn (Bennett *et al.*, 1987).

Siltation and metal contamination of the river system also arose due to the erosion of the tailings dump by monsoonal rains and flood waters (Bennett *et al.*, 1987; Lowson *et al.*, 1987). The average metal contents of these tailings were; 6000 mg/kg Cu, 1000 mg/kg Pb, 50 mg/kg Zn, 470 mg/kg U and 26000 Bq/kg Ra (Lowson *et al.*, 1987). To prevent erosion of the tailings into the river-system and to inhibit sulphide oxidation, the tailings were excavated and dumped into one of several large water-filled, open-cut pits on the site (Bell *et al.*, 1989). The land on which the tailings were originally deposited was treated with 8 tonnes of hydrated lime per hectare and covered with 300 mm of topsoil. The soil cover was then fertilised and sown with a mixture of tropical grasses, native shrubs and trees (Bennet *et al.*, 1987; Bell *et al.*, 1989).

Reclamation of the overburden wastes dumps at Rum Jungle involved recontouring the heaps and capping them with clay and soil materials to reduce the infiltration of water and to facilitate plant establishment. Considerable research was conducted investigating the effectiveness of the vegetated covers at reducing water infiltration, oxygen ingress and ultimately sulphide oxidation within the tailings (Bennett *et al.*, 1987; Harries & Ritchie, 1987, 1988). Although the primary purpose of the compacted clay cap was to abate the generation of AMD by restricting the ingress of water and oxygen into the sulphide-bearing wastes, the cap also helped to prevent contamination of the overlying soils by reducing capillary rise of acid and metal contaminated pore waters. The clay/soil barriers used on gently sloping areas of the Rum Jungle dumps consisted of a ≥ 225 mm layer of compacted clay, followed by a minimum of 250 mm of clayey sand (plant root zone), which was in turn overlain by 150 mm of gravelly sand (erosion control layer).

Whilst the results of reclamation work conducted at Rum Jungle appear very encouraging to date, only time will reveal how effective Australia's costliest rehabilitation program has been at curbing problems associated with sulphide oxidation.

3.2.1.2 Captains Flat, New South Wales

In terms of mineralogy, climate and history the Captains Flat Mine is similar to the Tui Mine. Captains Flat Mine is a former Au, Cu, Pb and Zn mine located 50 kilometres upstream of Canberra on the Molongolo River, in New South Wales. Mining was carried out at this site between 1874 and 1962 (Craze, 1977; Bell *et al.*, 1989). In contrast to Rum Jungle, rainfall at the site (740 mm/yr) is relatively well distributed throughout the year and mean monthly temperatures range from 20°C in summer to 6°C in winter. Despite being appreciably drier the climatic conditions at Captains Flat mine site are comparable to those at the Tui mine site in New Zealand (Chapter 2, section 2.3).

In a process similar to that which was used at the Tui mine site, metals were extracted from the crushed ore using froth flotation methods. The tailings were separated into fine and coarse fractions and disposed of in rudimentary earth dams and dumps respectively. By the time the mine closed, an estimated 15 ha of land was effectively covered by tailings (Bell *et al.*, 1989). Not only were the tailings unsightly, they were also a source of air and water pollution. The tailings exhibited similar characteristics to the Tui tailings in that they had a pH of less than 3.0 and contained high concentrations of sulphidic Cu, Pb and Zn. The tailings also generated AMD which effectively sterilised the Molongolo river for many kilometres downstream and even impacted water quality within Canberra lakes. After several unsuccessful attempts (c.1961) to chemically stabilise the tailings dams (which on several occasions partially collapsed into the Molongolo River), a concerted campaign was finally mounted in 1974 to investigate full reclamation of the site (Anon., 1974).

Initial field trials found, that despite the application of high rates of lime (40 - 50 t/ha) and compound fertilisers, vegetation failed to establish satisfactorily on the amended tailings (Craze, 1977, 1979). Following extensive laboratory, glasshouse and field trials, a decision was made to recontour the tailings dumps and to cap them with a clay/soil

cover capable of supporting plant growth. To reduce erosion and to facilitate revegetation and adequate drainage, the dumps were recontoured to produce terraced slopes with grades of between 5% and 33% (Bell *et al.*, 1989). The terraced slopes were then covered with 220 mm of compacted clay to inhibit air and water ingress into the tailings. This barrier was in turn covered with 450 mm of shale rock designed to inhibit capillary rise of contaminated water from the underlying clay cap and tailings into the plant root zone and to facilitate lateral water drainage. A 300 mm layer of locally sourced soil material was placed at the surface of the dam to host vegetation. The reconstituted soil was subsequently fertilised and sown with a grass/legume mix which included common pastoral species such as *Agrostis capillaris* and *Trifolium repens*. *Secale cereale* was also included as a nursery crop. After sowing, the soil surface was covered with a bitumen-based straw mulch and sprinkler irrigation was installed to ensure that water was non-limiting. Maintenance of the site included fertiliser dressing and the periodic slashing of pasture to encourage tillering. The reclamation of the site is estimated to have cost in the vicinity of \$3.5 million but has thus far shown very promising results (Bell *et al.*, 1989).

3.2.1.3 Mount Isa & Broken Hill

The climatic conditions prevailing at the Mount Isa and Broken Hill mine sites contrast with those at Rum Jungle and are significantly drier than those at the Captains Flat. Reclamation efforts at both sites are primarily governed by the arid climates in which evaporation greatly exceeds rainfall throughout most of the year. Summer temperatures at both sites commonly exceed 30° C and the availability of water during the height of summer is clearly an important factor limiting the establishment of plants on less than optimal growing media.

Although a variety of wastes are present at Mount Isa and Broken Hill, the reclamation of sulphidic base-metal tailings at each site has been the focus of considerable effort over the past few decades. Tailings at both sites are characterised by fine grain-size, low permeability, high bulk density, excessive salinity and low levels of nitrogen and phosphorus. Attempts to reclaim them have been aimed at controlling wind blown dust and to improve the appearance of the sites (Hunter & Whiteman, 1975; Bell *et al.*, 1989). Tailings at Broken Hill exhibited neutral to slightly alkaline pH due to the

addition of alkaline material during processing and to the predominance of what Bell *et al.* (1989) described as ‘inactive sulphides’. The pH of the Mount Isa tailings was similarly near neutral. Dolomite present in the tailings is believed to actively neutralise acid generated from the oxidation of pyrite.

Whilst research into the reclamation of tailings dams first began at Mount Isa in the 1960’s, the site is still very much operational and the deposition of tailings into several active dams continues. It is estimated that one of the dams currently in use will upon completion early next century, cover an area of 1400 ha and contain some $100 \times 10^6 \text{ m}^3$ of tailings (Bell *et al.*, 1989).

Trials used to assess vegetation establishment techniques at Mt. Isa and Broken Hill mine sites have met with mixed success over the years. Vegetation was established on about 30 ha of tailings at Mt Isa, however, during the early 1980’s via the use of trickle irrigation, pH amendment (fly ash) and the emplacement of a 0.3 to 1.0 m ‘rock’ cap over the tailings. A variety of exotic and native shrubs and grass species were then used to revegetate the material. Further discussion of this and other trials conducted at the two sites is outlined by Bell *et al.* (1989) in a useful review paper of mine tailings reclamation in Australia.

3.2.2 New Zealand Mine Sites

As briefly discussed in Chapter 2 (section 2.9), up until 1991 the 1971 Mining ^{Act} was the principal Act governing the extraction of Crown-owned minerals and the reclamation of land disturbed by mining in New Zealand. Prior to 1971 there were few environmental restrictions placed on mining companies and providing the criteria of the Water and Soil Conservation Act of 1967 were met, mining was carried out with little regard for the environment or the future use of the land. Thus, in terms of environmental protection, the Mining Act was an important piece of legislation in that it aimed to reduce environmental degradation associated with mining and forced mining companies to take some responsibility for the reclamation of mined land.

The passing of the Crown Minerals Act and Resource Management (RMA) in 1991 effectively tightened environmental controls governing mining activity in New Zealand

and was designed to minimise the likelihood of large scale environmental degradation resulting from mining activity in the future. The RMA requires mine practitioners to ‘avoid, mitigate or remedy’ any adverse effects of activities on the environment. Environmental damage is an inevitable consequence of many mining operations but has the greatest potential with large scale open-cast mining and/or with metalliferous mines which involve the extraction and processing of highly sulphidic ore.

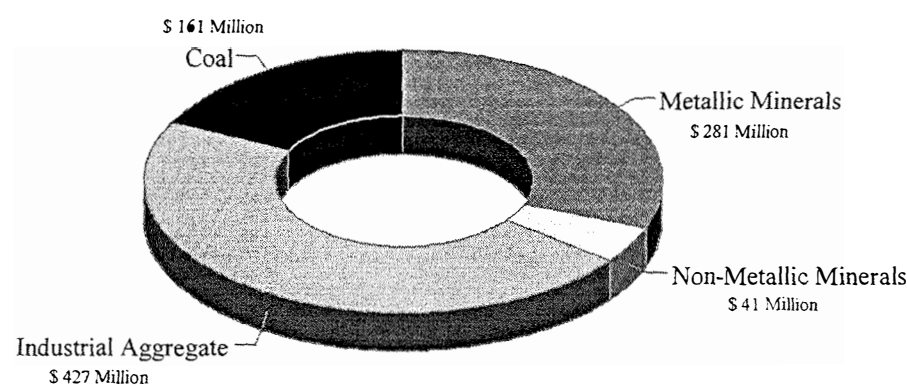


Figure 3.1 Economic importance of various mined materials in New Zealand in 1995.
(source: Ministry of Commerce, 1996)

As previously discussed in Chapter 2 (section 2.8) the mining of metals, particularly gold and silver, has been an important industry in New Zealand. During the second half of the 19th Century gold was one of this country’s major export earners and although gold/silver mining is no longer a mainstay of the New Zealand economy, this industry is currently an important source of overseas revenues. According to the *New Zealand Annual Mining Review 1995* over 12.1 tonnes of gold, 27.8 tonnes of silver and over 2.3 million tonnes of magnetite were produced in New Zealand (Ministry of Commerce, 1996). The combined worth of these metals was estimated at over \$ 281 million (Figure 3.1).

The following section outlines the operation and reclamation strategies and measures employed at several major mine sites in New Zealand. In the case of alluvial gold mining, aggregate mining and coal mining, an overview of these industries is given in terms of their nature and the means by which land disturbed by these activities is generally reclaimed. An overview of the environmental problems associated with the Tui mine site is included, as is a summary of the limited research that has been conducted investigating possible reclamation strategies.

3.2.2.1 Martha Hill Mine, Waihi

Epithermal gold deposits were first discovered at Martha Hill in 1878 and by 1912 the mine was reported to be the *'eleventh most productive mine in the world in terms of bullion won, and the second...in terms of greatness and stability'* (Moore *et al.*, 1996). Production continued at the mine until 1952 when it was forced to close down due primarily to declining gold prices. A dramatic increase in gold prices in the 1970s renewed interest in Martha Hill and mining finally resumed at the site in 1988. Annual gold and silver production levels are currently in the vicinity of 75000 oz (2100 kg) and 590000 oz (16700 kg) respectively (Moore *et al.*, 1996).

The open pit at Martha Hill is situated near the centre of Waihi township, an historical mining centre and service town for surrounding agricultural and horticultural enterprises. The present day mining operation involves conveying andesitic overburden and ore from the pit to a waste disposal area and processing plant situated 2.3 kilometres away which currently covers a ground surface area of 170 ha. Oxidised waste rock from the pit has been used to engineer a tailings dam embankment within which unoxidised (pyritic) waste rock has been buried in sealed 'cells' (Gregg *et al.*, 1995). Finely ground tailings consisting of sand, silt and clay sized particles from the treatment plant are transported as an aqueous slurry to the tailings impoundment where they are generally deposited sub-aerially via a series of spigots. The construction of a second, smaller tailings impoundment, to be situated immediately to the south-east of the existing dam, is likely to commence within the next few years.

The close proximity of the gold mine to Waihi township and stringent environmental controls outlined in the mining licence ensured that the planning and implementation of

reclamation of disturbed land was given high priority from the onset of mining. Gregg & Stewart (1991) perceived reclamation of the waste disposal area to be of particular importance, not only for aesthetic reasons but also because of its situation on productive farmland, formerly used for dairying.

In preparation for a mining licence Waihi Mining Company Ltd. was required to prove that the tailings and waste rock could be restored to levels of production at least equal to that of soils present at the site. Baseline studies identified that the existing productivity of soils to be impacted by mining ranged between 12000 and 16000 kg dry-matter per year (Mason *et al.*, 1995). A preliminary study was undertaken to investigate the physical and chemical properties of the tailings and wastes materials (both oxidised and unoxidised sulphide bearing rock) in terms of their plant growth properties (Widdowson *et al.*, 1984). The tailings were identified as comprising poorly aggregated, predominantly silt-sized particles with good moisture holding capacity but poor aeration and drainage. Chemically the tailings were found to be deficient in N, P and K and to exhibit low CEC and high pH (≈ 9). Despite these limitations, glasshouse trials demonstrated that once nutrient deficiencies were corrected, pasture plants could be successfully grown in tailings material. Similarly, the oxidised waste rock was found to show good potential as a plant growth medium provided it was adequately limed and fertilised. The unoxidised (pyritic) waste rock in contrast, was identified as an unsuitable plant growth medium due to its excessive soluble aluminium and salt content and high iron sulphide content (Widdowson *et al.*, 1984).

The initial engineering design proposed to strip between 100 and 150 mm of topsoil only from the tailings dam site prior to mining for resurfacing the bund and tailings pond (Gregg *et al.*, 1995). A surrogate subsoil was to be used on the tailings dam embankment and comprised of waste rock only. To investigate what depth of topsoil (if any) was required and whether oxidised waste was a suitable subsoil 3 field trials were set-up in 1985 (Gregg *et al.*, 1990; Horne *et al.*, 1990). The growth potential of tailings and waste rock amended with 4 depths of soil (0, 50, 150 & 250 mm) were assessed and compared to pasture production from both disturbed (topsoil removed and replaced) and undisturbed soil plots located next to the proposed waste disposal site (Gregg *et al.*, 1995).

(i) Tailings Trials

Pasture plots (10 m²) established on tailings amended with the varying depths of topsoil and 150 kg P/ha, 160 kg K/ha and 180 kg S/ha applied as potassic superphosphate in the first year, showed comparable levels of production to non-disturbed soils within 2 years of sowing (Gregg *et al.*, 1990). On average, yield differences between topsoil treatments for the first 5 years of the field trial were small, with the nil soil treatment performing well. Dry matter yields were, however, found to decrease significantly as the harvesting frequency of the trials was reduced.

In 1992 a study was carried out to investigate the rate of soil formation and nutrient status of the nil soil treated tailings (Gregg *et al.*, 1995). After 6 years of growth the pH of the tailings was found to have decreased from 9.2 to 6.0 and carbon and nitrogen levels had increased about 6 and 7 fold respectively. Mason *et al.* (1993) estimated that if C and N increases remained linear it would take about 24 years for C and N levels to reach those of the control soil (an undisturbed soil at the mine site used to gauge productivity).

Additional field trials were set-up in 1992 to investigate the amendment of tailings with locally sourced municipal compost. Pasture was established on sixteen 2 x 4 m plots, 8 of which were treated with 50 mm layer of compost. In a separate trial of similar design a variety of native plant species were trialed including, kohuhu (*Pittosporum tenuifolium*), kanuka (*Leptospermum ericoides*), cabbage tree (*Cordyline australis*) and flax (*Phormium tenax*) (Mason, 1996).

Mason (1996) once again found that the tailings exhibited few limitations to plant growth, however, compost addition was found to significantly improve pasture yields by improving P status. During this trial significantly higher yields of pasture (14000 kg cf. 6000-7000 kg dry-matter/ha) were obtained off the compost amended tailings compared to tailings amended with a similar depth of soil in the previously outlined trial of Gregg *et al.*, (1990). These differences were attributed to the superior P status of the compost amended treatment and differences in seasonal rainfall variation (Mason, 1996).

In the case of native plants, compost was found to improve growth in the first 6 months, but beyond 6 months no significant yield differences were observed between the nil compost and compost treated plots (Mason, 1996). In the presence of slow release fertilisers growth rates of the various native species were all very promising, suggesting that reclamation of tailings with native vegetation is a feasible long term option (Mason, 1996).

(ii) Tailings Reclamation Strategies

Reclamation strategies for reclaiming the surface of the existing tailings dam, upon decommissioning of the Waihi mine, include using the area as a waste rock disposal area, leaving the area flooded, capping the entire dam surface with a dry cover such as clay or compost, or using a combined water/cap cover (Mason, 1996). Whilst none of these options have been ruled out it is probable that reclamation of the dam will involve the later option (combined water/cap covers). Such a cover is likely to involve the capping of higher strength (coarser) tailings near the impoundment's perimeter with a composite waste-rock and soil cover and maintaining a water body over very finely ground tailings which take considerable time to consolidate and thus to develop shear strength. This type of cover would potentially improve stability of the dam crest, reduce soil material requirements for capping purposes, accommodate consolidation of the tailings and potentially provide an aesthetically attractive wetland and recreational area. Predictive modelling suggests that the reclamation of capped areas to pasture would be less costly and would require less maintenance than reclamation to native plants (Mason, 1996).

It is highly unlikely that the surface of the dams will be sealed in an attempt to prevent water and air infiltration into the tailings. Such measures are likely to be prohibitively expensive and unnecessary given the low toxicity of the tailings. The Waihi tailings differ markedly from the Tui tailings, in that they contain relatively low concentrations of acid generating pyrite as indicated by their low total sulphur content ($<0.0015\%$). In addition, the Waihi tailings generally contain comparatively low concentrations of most heavy metals and exhibit alkaline pH (Widdowson *et al.*, 1984; Gregg *et al.*, 1995).

(iii) Waste Rock Trials

In addition to investigating the growth response of pasture species grown on oxidised waste rock amended with 4 depths of soil, the underlying waste-rock on half of the sixteen 30 m² plots was modified with lime (6 Mg/ha) and superphosphate (1 Mg/ha). A full discussion of the trial which yielded some interesting results is detailed in Gregg *et al.* (1990 & 1995). In short, modification of the waste rock with lime and superphosphate substantially increased yield by almost 4000 kg of dry matter per hectare in the first year of the trial. It was assumed that the lime and superphosphate treatment reduced phytotoxic levels of soluble aluminium in the surrogate waste subsoil, although improved P status may have also encouraged plant growth. Surprisingly, where no topsoil was used, the highest level of pasture production occurred due to what was assumed to be a more favourable P status. Less weeds, however, and lower populations of soil borne pathogens may have also aided plant growth on this treatment. By the third year of the trial no differences in pasture production between the modified and unmodified waste treatments were evident (Gregg *et al.*, 1990, 1995). Research conducted by Gurung *et al.* (1996) indicates that the reduced yield differences between the modified and unmodified waste rock arose due to the progressive leaching of organic ligands (produced by the decomposition of organic matter) which complexed toxic Al within the waste rock.

The results of initial trial work carried out at the mine site indicated that both waste rock and overlying soil were well suited to plant growth providing they were adequately limed and fertilised. Although the waste rock was found to have limited ability to store water (Horne *et al.*, 1990), this was not anticipated to be a major limitation to plant growth due to the site's high and regular rainfall (c.2500 mm/yr). Gregg *et al.*, (1990), however, considered that 'high' inputs of fertiliser and well managed grazing of the restored soils were imperative to avoid pasture regression, soil compaction and erosion. They further suggested that in the first 3 to 5 years of pasture production, grazing use of the land should be dictated by pasture availability and soil condition and not by animal feed requirements.

Progressive reclamation of the bund area has been commenced as per a condition of the mining licence and to date (July 1997), over twenty hectares of the waste bund have been successfully revegetated using methods developed from the various trial work. The reinstatement of pasture on the bund currently involves ripping and amending the surface waste rock with lime (6000 kg/ha) and superphosphate (1000 kg/ha) prior to the addition of 100 mm of previously stripped and stockpiled topsoil. The soil cover is then topdressed with 1400 kg/ha of 5% potassic superphosphate (and limed if required) and sown with ryegrass and clover species at a rate of 40 kg/ha. The use of low ground pressure machines and a subsoiler in the placement of subsoils ensures compaction is minimised and root penetration and drainage between the horizons is improved (Lapwood, 1991).

Ongoing research at Martha Hill goldmine investigating pit wall revegetation and reclamation options for the tailings disposal area, combined with stringent management practices and environmental controls is likely to ensure the long-term success of reclamation efforts at this site.

3.2.2.2 Golden Cross Mine, Waihi

Golden Cross is a combined open-pit/underground hardrock gold mine situated 8 kilometres NW of Waihi. Whilst small areas of land at the mine site have been revegetated with exotic grasses and native plant species, large scale reclamation of the site will not be undertaken until the end of the mining project (Bokich, 1995). Upon closure of the mine (originally projected to be in the year 2001) it is anticipated that most disturbed areas will be revegetated with native plant species (Bokich, 1995; Raea, 1997). The general aim of reclamation at the site will be to stabilise soils and to prevent the generation of AMD from mine workings and sulphide-bearing wastes (Bokich, 1995).

The tailings embankment at Golden Cross is currently being constructed from overburden waste rock from the open pit. Highly sulphidic wastes are either blended with benign waste rock and compacted to a permeability of 1×10^{-8} m/s or encapsulated within compacted fine grained wastes to help prevent oxidation (Bokich, 1995, Weston, 1995). Prior to deposition within the impoundment, the tailings produced by the

goldmining venture are treated to remove cyanide and limed to pH 9.5 to encourage the formation of highly insoluble metal complexes (Bokich, 1995). Upon closure of the mine the company intends to rehabilitate the tailings pond to wetlands which will maintain a reducing environment (Bokich, 1995).

Recently, reclamation efforts at Golden Cross have been drawn into the media spotlight following revelations that the tailings dam, which contains over 3.0 million tonnes of tailings, is situated on unstable terrain (Raea, 1997). Land immediately adjacent to the tailings dam has begun to slowly move due to the activity of a deep seated fault within underlying strata (Crampton, 1996; Maré, 1997; Raea, 1997). Coeur Gold New Zealand Limited¹, who manage and own 80% of the mine, first publicly announced that there were potential problems with the dam's stability in November 1995 (Weston, 1995; Crampton, 1996). Since that time the company has reputedly spent \$20 million dollars in attempts to stabilise the site (Maré, 1997; Raea, 1997).

Remedial works undertaken at Golden Cross include the excavation of a 1 km drainage tunnel and 100 horizontal boreholes to dewater failing strata, the construction of rock buttresses and ongoing reduction of water levels within the tailings impoundment (Crampton, 1996; Maré, 1997). Upon notification of the stability problem, the Waikato Regional Council ordered Coeur Gold to investigate the feasibility of relocating the dam. It is estimated that if such measures were required it would cost the company more than \$100 million (Raea, 1997). To date environmental bonds totaling \$12.1 million have been signed by Coeur Gold New Zealand Limited to ensure that the company does not 'abandon' the site. Obviously any efforts at rehabilitating the tailings dam are likely to take a back seat to insuring its long term stability.

3.2.2.3 Macraes Flat Mine, Eastern Otago

The Macraes Flat Mine is New Zealand's largest and currently most profitable goldmine. It is located approximately 60 kilometres due north of Dunedin on the eastern edge of the Otago Goldfield. In 1996 the mine produced 138,464 oz (3925 kg) of gold from chlorite schist-hosted quartz lodes (Gregg, 1997). The majority of ore mined at

¹ Coeur Gold NZ Ltd. are a fully owned subsidiary of Idaho based Coeur d'Alene Mines Corporation.

Macraes contains appreciable quantities of sulphide minerals including pyrite, arsenopyrite and minor chalcopyrite. Gold is recovered from the ore using cyanide and activated carbon processing. The finely ground tailings are pumped into a dam adjacent to the processing plant where they are left to dewater. As with the Golden Cross dam, the primary tailings dam at Macraes Flat is engineered to withstand a Maximum Credible Earthquake for the region (Crampton, 1993; Gregg, 1997).

The objectives of reclamation at Macraes is to progressively rehabilitate the mined land to a state compatible with the landscape and the environment that existed prior to mining activity (Gregg, 1997). The shallow soils, low rainfall and temperature extremes at the site present challenges to the mining company in terms of meeting these goals and rehabilitating the site. The revegetation of the tailings dam(s) upon completion of mining activity is likely to involve the ‘replacement’ of topsoil that has been excavated and stockpiled from stripping areas. Whilst the arid conditions at the site preclude the likely production of large volumes of AMD, sulphide bearing wastes will have to be managed appropriately and capped where necessary to minimise sulphide oxidation.

Despite ongoing expansion of the site, significant areas have already been revegetated using pastoral plant species consistent with that of land surrounding the 400 ha licensed area. Trials are currently being carried out to identify the most appropriate combination of vegetation to be used for reclamation. Additional trials are planned to investigate the suitability of various native shrub and tree species for revegetating steeper slopes at the site (Gregg, 1997).

3.2.2.4 Alluvial Gold Mine Reclamation

It is estimated that there are about 60 active alluvial mining licences working gold-bearing gravels and sands in New Zealand (Davidson, 1997). The majority of these placer deposits occur in fluvio-glacial gravels, uplifted beach deposits and in Holocene river gravels and beach sands in Westland and Otago (Christie & Brathwaite, 1997). The Grey river dredge operated by Birchfield Minerals Ltd. is currently the largest alluvial goldmine in the country employing 24 full-time staff (Davidson, 1997). Other relatively large operations include Arahura Valley, Jones Flat, Mikonui and Nokomai (Mineral Resources, 1997). Alluvial gold production from these and numerous smaller operations

currently accounts for about 25% of the total gold produced in New Zealand. Conservative estimates suggest that the alluvial gold resource in Westland is over 300 tonnes and about 100 tonnes in Otago (Davidson, 1997).

As previously discussed, up until the introduction of the Mining Act in 1971, mining legislation in New Zealand poorly protected the environment against large scale degradation associated with alluvial gold and other forms of mining. The Kanieri Dredge, for example, described by Fricker (1986) as the ‘last of the leviathans’, operated for 44 years, during which time the dredge won over 420,000 oz (c.12,000 kg) of gold from alluvial gravel deposits in the Kanieri and Taramakau river systems (Gregg *et al.*, *in press*). For 39 years the company operating the dredge was not obliged to reclaim land disturbed by the mining operations. Clauses in the mining legislation of the time provided a ‘no reclamation’ option in which companies could pay a flat fee of \$75 per hectare in lieu of reclamation (Gregg *et al.*, *in press*). As a consequence of this legislation large tracts of land were left highly degraded by the Kanieri and other dredging operations in Westland and Otago. In Westland, herring bone heaps of coarse tailings interspersed with dredge ponds disrupted natural water courses and replaced natural river flats and terraces, many of which supported podocarp forests prior to mining (Gregg *et al.*, *in press*). About 3000 ha of land is estimated to have been highly degraded by alluvial dredge operations in Westland and Central Otago over the last 100 years or so (Fricker, 1986).

The manner in which the Kanieri and other early dredging operations processed alluvial gravels often resulted in the burial of fine-grained tailings and elevation of mined land (often by as much 4 to 6 m) due to swelling arising from the poor mixing of tailings fractions upon redeposition (Gregg *et al.*, *in press*). Such operations effectively reduced ground water levels and resulted in the deposition of coarse tailings with low water holding capacity and nutrient status at the ground surface. Despite Westland’s high rainfall these factors made the material prone to drought and inhibited natural revegetation of the tailings by most plant species for periods in excess of 20 to 80 years (Ross & Mew, 1991; Gregg *et al.*, *in press*).

Changes in the legislation in 1971 forced the mining companies to begin rehabilitating disturbed land to a state at least as productive as its pre-mine state. The legislation change prompted a surge in reclamation research associated with the alluvial gold-mining industry. Much of the research conducted at West Coast alluvial mine sites concentrated on the reclamation of tailings to exotic forestry and/or pasture. White pine (*Pinus radiata*) and Douglas fir (*Pseudotsuga menziesii*) were two exotic tree species that were trialed along with a variety of legume and grass species (Keating & Buckley, 1981; Fitzgerald, 1981; Ross, 1988; Frazer & Keoghan, 1990; Metcalfe & Godfrey, 1990; Morton & Harrison, 1990; Ross & Mew, 1991; Gregg *et al.*, *in press*).

Useful literature pertaining to the reclamation of alluvial gold tailings to forestry and pasture in New Zealand are given by Ross & Mew (1990), Mew & Ross (1991), and to indigenous vegetation by Norton (1991) and Mew & Ross (1992a). It is generally considered that thorough site assessment, early planning and careful consideration of post mining vegetation are of paramount importance in ensuring that problems associated with reclamation are minimised. Research also indicates that revegetation is usually best achieved by redepositing stripped topsoil onto mixed tailings substrates. Furthermore, the contouring of soils and the replacement of debris (eg. logs and stumps) to provide micro-sites for establishing seedlings, has also been shown to aid the establishment of trees and shrubs. In the case of pasture, well managed grazing, fertiliser topdressing, weed and pest control are considered to be critical post reclamation practices (Ross & Mew, 1990; Mew & Ross, 1991).

To date, there has been mixed success establishing vegetation on 'abandoned' alluvial gold dredge tailings. Whilst the productivity of land at some sites surpasses pre-mine levels, other attempts at revegetation have been unsatisfactory (Ross & Mew, 1990; Mew & Ross, 1991). Reclamation efforts on recent tailings derived from the Grey River Dredge are reportedly "*gratifying*" in that the quality of established pasture has exceeded expectations (Davidson, 1997). Clearly continuing research will ensure that future alluvial mining will have far less impact on the environment than have past operations. It is likely that research into the reclamation of tailings to indigenous vegetation will be of high priority in Westland, particularly in areas administered by the Department of Conservation (Norton, 1991).

3.2.2.5 Titanomagnetite Mining, Waipipi

The mining of titanomagnetite minerals from coastal sands in Taranaki region commenced in 1971. Waipipi Ironsands Limited mined more than 800 ha of land over a period of almost 2 decades. The mining operation was carried out on 2 distinct physiographic units, (i) coastal sand dunes with weakly developed, shallow (60 mm) topsoils and (ii) sand flats characterised by deeper topsoils and gleyed subsoils hosting iron pans and concretions (Gregg *et al.*, *in press*). The carrying capacity of the 2 units before mining ranged from 3 to 8 su/ha on moderately to steeply sloping sand dunes, to 12 su/ha on the sand flats (Gregg *et al.*, *in press*).

Reclamation of mined land to pasture was generally conducted using the following technique. Prior to mining 0.3 to 0.5 m of soil material was bulldozed to the sides of the dredge's path where it was stockpiled for up to 4 months. After the removal of the titanomagnetite by wet concentration from the crude sands, the tailings² were pumped back into the dredge pond and left to settle and dewater before being recontoured by bulldozers. The soil material was then respread over the levelled tailings and sown with a 50:50 nursery crop of barley (*Hordeum vulgare*) and oats (*Avena sativa*) at a rate of 115 kg/ha (Gregg *et al.*, *in press*). This vegetative cover was designed to rapidly stabilise the erosion-prone tailings. When the cereal crop reached a height of about 0.25 m it was over-sown by 40 kg of a grass/clover seed mix using a direct drill seeder. Included in the mix were white clover (*Trifolium repens*), tall fescue (*Festuca arundinacea*), cocksfoot (*Dactylis glomerata*), canary grass (*Phalaris tuberosa*) and type specific rhizobium. An NPKS (12:10:10:8) compound fertiliser was applied at a rate of 150 kg/ha at each sowing. The reclaimed land was generally fit for grazing within 18 months of mining (Gregg *et al.*, *in press*).

During operations at Waipipi some 800 ha of land was rehabilitated to farmland which was generally more versatile and productive than the original farmland (Taylor & Walker, 1987; Gregg & Stewart, 1991; Gregg *et al.*, *in press*). The success of reclamation at the site is attributable to the area's well distributed rainfall (c.950 mm/yr) and to the company's commitment to reclamation research from the onset of operations.

² Gangue minerals within the tailings were primarily augite, hornblende and plagioclase feldspars with minor hypersthene, olivine, quartz, garnet, apatite and zircon (Gow, 1987)

Several research projects were conducted at Waipipi including trials that investigated topsoil/subsoil stripping, fertiliser application, crop harvest, the performance of lucerne (*Medicago sativa*) and kikuyu (*Pennisetum clandestine*), conservation tillage trial, rotational grazing and weed control and animal nutrition (Bruere, 1981, Gregg, 1983; Gregg & Stewart, 1991; Gregg *et al.*, *in press*). The results of this research provided the company with valuable information and enabled it to deal with problems encountered during the course of the operations. Problems associated with excessive drainage and stock copper deficiencies for example, were identified and remedied by changes in practice (Gregg *et al.*, *in press*).

Recontouring (flattening) of the land and the sowing of improved pasture species were primary factors which enabled the land to be used more intensively. The stock carrying capacity of much of the mined land was doubled as a result of the reclamation techniques employed at Waipipi (Gregg *et al.*, *in press*).

Mining operations ceased at Waipipi in c.1988, however, ironsand is currently being mined at Taharoa and at Waikato North Head on the west coast of the North Island. Over 2 million tonnes of magnetite with an estimated value of \$23 million dollars were produced from these sites in 1995 (Ministry of Commerce, 1996).

3.2.2.6 Aggregate Mine Reclamation

In terms of both volume and monetary worth, aggregate mining is the largest extractive industry in New Zealand. In 1995, the mining of aggregate material (chiefly sand and rock used for building and roading) accounted for about 47% of mineral production and was valued at over \$426 million (Figure 3.1). Some 23 million tonnes of aggregate were mined from a variety of sources including, the greywacke rocks of the ranges in both the North and South Islands, river gravels particularly in the south of the North Island and throughout the South Island and volcanic rocks (mainly basalt and andesite), particularly in the north of the North Island and near Christchurch and Dunedin (Simcock, 1995; Ministry of Commerce, 1995).

Given the variable lithology, climate and topography of land hosting aggregate resources it follows that the scale and extractive nature of aggregate mining varies considerably

about the country. Whereas hardrock quarries are often located in steep terrain that host shallow soils and low quality pasture and/or scrub, some of New Zealand's most fertile and versatile soils mantle equally important reserves of alluvial aggregate (McQueen, 1983; Simcock, 1993; Simcock & Ross, 1995).

To date there have been only 3 major studies conducted in New Zealand investigating the reclamation of aggregate mines (McQueen, 1983; Duck & Burton, 1985; Simcock, 1993). This is a surprising fact given the potential impact and economic importance of the industry in New Zealand. The studies all identified that aggregate mining could seriously impact the long-term productivity of land and that soil/substrate compaction, topsoil dilution and inadequate topsoil depth were common problems mitigating against successful revegetation. Simcock (1993), however, found that acceptable levels of vegetative production (comparable to pre-mining levels) could be achieved by stripping and replacing topsoil and subsoils separately using a hydraulic excavator to minimise compaction. The study highlighted that different reclamation techniques were required for different soils. Simcock & Ross (1995) suggest that the segregation and 'burial' of poorly drained material and the use of progressive reclamation are also key factors in maximising plant growth and minimising soil structural degradation associated with organic matter depletion.

3.2.2.7 Coal Mine Reclamation

In terms of volume extracted, the coal mining industry is the second largest mining industry in New Zealand. The combined production of New Zealand's coal mines in 1995 was 3,445,038 tonnes of mainly bituminous and sub-bituminous coal valued at about \$161 million (Ministry of Commerce, 1996). Even by international standards New Zealand's recoverable coal resources (8600 million tonnes) are substantial in size. The vast lignite deposits of Otago and Southland make up the bulk of these reserves (7055 million tonnes) and are New Zealand's largest known energy resource (Ministry of Commerce, 1995).

Waikato in the North Island and Westland in the South Island are New Zealand's two primary coal mining districts. Bituminous coal reserves are concentrated in the West Coast's Buller and Grey coalfields, whereas the nation's largest sub-bituminous

resources occur in the Waikato region. Among the largest producing coal mines in New Zealand are Stockton, Webb, Wairaki and New Vale in the South Island and the Huntly East, Maori Farm, Waipuna and Kopuku mines in the North Island. The combined production from these mines in 1994 was over 2 million tonnes of coal (Ministry of Commerce, 1995). New mines recently commissioned include the Mount Davy mine near Greymouth and the Kopako III mine near Maramarua, 30 kilometres east of Huntly (Mineral Resources, 1997).

Coal was first commercially mined in New Zealand in the 1830's and remained the Country's primary energy source for the next 100 years. The OPEC oil crises of 1973 and 1974 renewed interest in New Zealand's coal resources. Detailed surveys of New Zealand's coalfields were conducted between 1975 and 1987 and led, ultimately, to an increase in coal mining activity (Ministry of Commerce, 1995).

Traditionally, most coal in New Zealand has been mined using open-cast methods and currently only about 15% of coal is extracted via underground mining methods (Ministry of Commerce, 1995). Open-cast mining generally has far greater impact on the aquatic and terrestrial environment than underground mining and can potentially lead to major environmental problems, particularly where overburden contains high concentrations of pyrite. An increase in open-cast mining at Ohai in Southland c.1975 led to severe stream pollution from poorly managed and unvegetated pyritic overburden heaps and from uncontrolled discharges of acidic and metal contaminated waters. Strong public concern led to the reclamation of 90 ha of land at Ohai at a cost of \$5000/ha to control water quality at the site (Fricker, 1986). Similar environmental problems arose in the Waikato coalfield as mining activity increased in response to rising coal prices in the late 1970s. This prompted the industry in this region to more thoroughly investigate reclamation options and practices. Early coal mining operations on the West Coast have often been poorly regulated and managed. Fricker (1986) reported that as recently as 1986 some mines were discharging acidic mine wastes and/or effluent into local streams and using overburden disposal methods known to be detrimental to the environment.

Extensive trial work and increased awareness of the West Coast's fragile ecosystems has seen greater efforts being made by mining practitioners to adequately reclaim mine

sites and to minimise the discharge of AMD from sulphide-bearing overburden (Mew & Ross, 1992b; Davis *et al.*, 1995; Ross *et al.*, 1995; Simcock & Ross, 1995). One of the more innovative studies presently being conducted is a collaborative research project between Manaaki Whenua-Landcare Research, Forest Research Institute and Dunollie Coal Mines Limited at Giles Creek Coal mine (Davis *et al.*, 1995; Ross *et al.*, 1995; Simcock & Ross, 1995). The research focuses on developing techniques of establishing native vegetation on mine wastes, an area of reclamation that is considered to be poorly developed compared to reclamation using exotic forestry and pasture (Gregg *et al.*, 1990; Davis *et al.*, 1995; Ross & Mew, 1991; Simcock & Ross, 1995).

Giles Creek is situated in Westland, 12 kilometres north-west of Reefton and is a relatively small sub-bituminous coal mine with reserves estimated at 10 million tonnes (Mineral Resources, 1997). The mine is located in beech-podocarp forest which has been selectively logged for rimu and miro. Rainfall at the site is about 2900 mm/yr. Initial reclamation research began at the mine site in 1990 when trials were established on a capped overburden dump (Davis *et al.*, 1995). Despite good control of competing vegetation, native seedling mortality was high on the trial plots and plant growth rates were low. The poor performance of most native species was attributed to inadequate drainage caused by the fine-grained nature of the capping material. The trial highlighted that good drainage was a key factor governing the establishment of native woody species in a high rainfall environment. The results of the trial also demonstrated the necessity to provide adequate animal control to prevent excessive browsing. Good fencing and the use of low palatability species are important methods to prevent browsing (Davis *et al.*, 1995; Ross *et al.*, 1995).

Additional field trials were set up in 1992 at the site to study the methods and effects of soil replacement on the survival and growth of a variety of native tree and shrub species grown on overburden. The trial highlighted the need to strip and replace adequately drained soils, to minimise compaction and to ensure surrogate soils are adequately fertilised. Nitrogen was considered to be the most severe nutrient deficiency affecting plant growth (Davis *et al.*, 1995).

In response to trial results the company has begun salvaging tree stumps with attached soil material and replacing them on recontoured spoil to produce ‘instant forest’. The placement of stumps and forest debris is believed to “kick start” regeneration of native forest by supplying plant material, nutrients and shelter for establishing plants. This type of revegetation technique is well suited to sites containing existing native forest on terrain that allows heavy machinery access (Simcock & Ross, 1995). Simcock & Ross (1995) and Davis *et al.*, (1995) provide a useful review outlining the methods of restoring New Zealand native forests after mining and specifically cite the Giles Creek mine as an example of an integrated approach to site reclamation.

Although the reclamation research at Giles Creek is perhaps the most innovative coal mine reclamation research conducted in New Zealand to date, several other notable studies have been conducted. These include the studies of McQueen & Ross, (1982), Widdowson *et al.*, (1982), Ross & Widdowson (1985) and Widdowson & McQueen (1990). Informal trials have also been conducted by Solid Energy (formerly Coal Corporation) at mine sites around Huntly in the Waikato. Common factors identified in these studies shown to improve plant establishment were the need to:- (i) strip and replace topsoils and well drained subsoils where at all possible, (ii) minimise and/or ameliorate compaction and (iii) assess and rectify nutrient deficiencies. Clearly the appropriate handling and disposal of acid generating overburden is of paramount importance at sites where these materials occur.

3.2.2.8 Tui Mine, Te Aroha

The Tui Mine is a graphic example of a base-metal mine that was very poorly managed in terms of environmental impact. As discussed in Chapter 2 (section 2.8), the Tui Mine was first opened in 1884 but the bulk of the mine’s production occurred during the late 1960’s and early 1970’s. By the time the Mining Act (1971) was passed considerable environmental damage had occurred at the Tui mine site and the scene was set for continued degradation.

As outlined in Chapter 2 (section 2.8), the mining operation at Tui was carried-out underground and involved driving adits (horizontal drives) into the host rock. Upon interception of the quartz reefs hosting the sulphide ore, mining was redirected along the

reefs and high grade ore was selectively removed via adits which were developed on 5 levels and ranged in length from about 9 to 412 m (Carter & Pharo, 1965). The ore was transported from the mine adits to a flotation mill where it was first pulverised and then passed through flotation cells to physically concentrate the ore. The flotation process involved feeding finely-ground ore into a series of separation tanks containing water and a variety of oil reagents. The oil reagents were formulated to selectively coat one or more sulphide mineral components of the ore. Aeration of the mixture resulted in the formation of a metal-bearing ‘oil froth’ at the surface of the tanks which was removed to yield the metal-concentrate (Blaiklock, 1981; Brady & Humiston, 1982). The ‘differential’ flotation process used at the Tui mine site produced 2 concentrates, a zinc and cadmium concentrate and a lead and copper concentrate which also contained gold and silver (Norpac Mining Limited, undated).

Waste water produced from the ore processing was first decanted and then discharged “into a stream [the Tui Stream] specified by the local Borough Council” (Norpac Mining Limited, undated). Tailings from the mill are believed to have been deposited into the tailings dam as a thick slurry from a point source(s) immediately beneath the flotation mill. Photographs taken during the mine’s operation indicate that tailings were redistributed and levelled with a bulldozer (Cochrane, 1969). During the initial stages of the mine’s development the tailings were contained by a 5 m clay bund. This bund is situated beneath the front (western) face of the dam and is now covered by over 7 m of tailings (Tonkin & Taylor, 1974). Thus the bulk of the tailings are therefore not structurally contained by a purpose-built retaining wall such as that constructed at the Waihi waste disposal area.

The ‘on site’ problems associated with the Tui Mine are numerous and include:-

- a) *Visual impact* - aesthetically the unvegetated tailings dam, disused roads and abandoned plant degrade the landscape. The negative visual impact of these structures and particularly the tailings dam, contrasts strongly with the scenic native bush surrounding the mine site (Plate 2.1).

- b) *Water Contamination* - acid and/or heavy metal contaminated leachates emanating from the tailings dam and abandoned mine adits have severely polluted the Tui and the northern Tunakohoa streams (Plate 3.1). Pollution of the streams is most severe near the site and is exacerbated by the precipitation of ferric oxy-hydroxide which acts as a scavenger of heavy metals and contaminates the stream sediments (Ward *et al.*, 1976; Hendy, 1981; Pang, 1992).

- c) *Stream Choking* - debris in the form of tailings, waste rock and timber derived from the mining operation choke natural stream valleys and inhibit water flow (Plate 3.2). A severe rainstorm in 1971 reportedly caused the collapse of “several thousand tons” of material from waste rock dumps situated at the 2 lower levels of the mine. Debris from these dumps was carried into the northern Tunakohoa Stream, blocking culverts (WRCM, 1991). Mass movement and debris flows are known to be a serious hazard on the steep slopes of Mount Te Aroha particularly during periods of prolonged heavy rainfall (Arand, 1986).

- d) *Soil Contamination* - the studies of Ward *et al.* (1976, 1977) indicates that heavy metal (Cd, Zn, Cu, Pb) contamination of the surrounding area occurred via the airborne dispersal of dust particles derived from treatment plant during operations. It is highly probable that wind erosion of the tailings continues to contaminate land adjacent to the dam.

- e) *Tailings Instability/Erosion* - whilst an engineering study conducted in 1974 suggests that “*there is an adequate factor against an overall failure of the tailings dam*”, its structural integrity is considered to be dependent on the tailings remaining largely unsaturated (Tonkin & Taylor, 1974). Past events suggest that small scale slumping and erosion pose the greatest threat to the short-term stability of the tailings (Plate 3.3). Rainstorms in 1971, 1974 and 1976 reportedly caused severe rill and gully erosion of the tailings and led to surface flooding of the dam (Hansen, 1989; WRCM, 1991). Some have also voiced concerns about the possibility of the northern Tunakohoa Stream eroding laterally and undermining the long term stability of the tailings dam.

The major 'off site' problem associated with the Tui mine site is that of heavy metal contamination of water and sediments down stream of the mine site. As discussed in Chapter 2 (section 2.4) several studies have investigated the impact of mining operations local streams and ground water (Ward *et al.*, 1976; Tay, 1980; Hendy, 1981; Smith, 1986; Livingston, 1987; Pang, 1992, 1995). Whilst water quality improves with distance from the mine site as a result of ferric oxy-hydroxide precipitation and dilution by groundwater and tributaries, research indicates that the quality of water in the northern Tunakohoia and Tui streams is far from optimal at the streams' confluences with the Waihou River (Figure 2.1).

Of the two streams, the Tui Stream has been the most seriously impacted by past mining activity due to the inflow of AMD from the tailings dam (Table 2.1). As discussed in section 3.4, AMD is a serious problem that impacts many active and abandoned mine sites around the world where sulphide-bearing wastes are disturbed and exposed to oxidising conditions. The paucity of acid neutralising carbonate minerals in the finely-ground Tui tailings, combined with the tailings' comparatively high sulphide content and the site's high rainfall and warm climate, has led to the oxidation of substantial quantities of acid generating sulphide minerals and ultimately to the production of AMD. Water percolating through the tailings thus acts as a conduit of acid, sulphate and heavy metals into the Tui Stream (Ward *et al.*, 1976; Tay, 1980; Hendy, 1981; Pang, 1992). The capacity of the Tui mine tailings to continue to liberate AMD is considered to be the primary problem at the mine site (Miller, 1995, *pers. comm.*; Morrell *et al.*, 1995; EWM, 1995).



Plate 3.1 Metal contaminated drainage emanating from an adit at the Tui mine site. Precipitated ferric iron compounds are seen coating the rocks and mining debris (August 1993).



Plate 3.2 Rock and mining debris choking the upper reaches of the northern Tunakohoia Stream above the Tui tailings dam (August 1993).

(i) Past Reclamation Efforts/Research

To date no comprehensive attempts have been made to reclaim the Tui mine site or to remedy the impact of AMD and metal contaminated mine drainage on ground and stream water. Furthermore, surprisingly little practical research has been conducted to investigate potential methods of reclaiming the site. One of the few known studies to have specifically investigated a means of rehabilitating the site was conducted in 1975 (by the now defunct Hauraki Catchment Board) when field trials were set up to determine if pasture grass species could be established on the tailings dam (WRCM, 1991). Unfortunately and somewhat ironically, these trials (which were in part designed to investigate the ability of vegetation to stabilise tailings) were prematurely terminated by a rainstorm in September 1976 which is believed to have effectively washed the trials away. Documents detailing the location, design and results of these trials are not held by the Matamata-Piako District Council which raises the question of whether in fact they actually existed. Based on the limited information that is available, it appears that the trials were established on the tailings embankment and that vegetation was only ‘successfully’ established on those plots which received very ‘heavy’ applications of lime (Hansen, 1989; WRCM, 1991).

Following the 1976 rainstorm which destroyed the aforementioned trials and caused substantial erosion of the tailings embankment, the former Hauraki Catchment Board undertook measures to stabilise the tailings embankments and to “revamp” the drainage system to reduce the risk of blockage and saturation of the tailings (Hansen, 1989; WRCM, 1991). Amongst other measures implemented, the face of the dam (Plate 3.4) was ‘stabilised’ by covering it with a 15 - 20 cm layer of “*crushed quartz*” (Hansen, 1989). The placement of this cover³ was primarily designed to reduce rill and gully erosion of the tailings (Plate 3.3) . The capacity of the external drainage system which diverts catchment water around the tailings dam was also increased. Stabilisation and drainage work carried out at the site is believed to have cost the Hauraki Catchment Board in the order of \$75,000 (1989 estimate; Hansen, 1989). As mentioned in Chapter 2 (section 2.9), the National Government made a \$25,000 *ex gratia* payment to the Hauraki Catchment Board in 1981 to offset the costs of stabilising the dam. The current

³ As discussed in Chapter 4 (section 4.1), this material is thought to have originally had an appreciable sulphide content.

owners of the land upon which the Tui tailings dam is located, the Matamata-Piako District Council, are responsible for the ongoing maintenance of the site which costs and estimated \$2,500 per annum (1993 estimate; Tui Meeting, 1993).

The Waikato Regional Council and the former Hauraki Catchment Board have made preliminary investigations into the costs of possible options for reclaiming the Tui mine site. Amongst the options initially investigated was the relocation of the tailings dam. In 1979 it was estimated this would cost in the vicinity of \$200,000 however, no alternative location was suggested (WRCM, 1991). This option is highly unlikely to ever be implemented unless a 100,000 m³ sinkhole conveniently forms near the mine site (a somewhat highly improbable scenario given the non-calcareous lithology of the region!).

Options considered for mitigating contamination of the Tui and northern Tunakohoa Streams by heavy metal-contaminated drainage, included intercepting drainage from each adit and piping it to a central treatment facility along with the tailings' leachates. Carter (1981) suggested that the yearly running cost of such a facility would be between \$600,000 and \$1,000,000. Another option considered to prevent contamination of the northern Tunakohoa Stream by mine adit drainage was to seal and flood the underground mine workings (Fyson, 1991; WRCM, 1991). This option was recognised as requiring a large scale geotechnical investigation and approval from the Ministry of Commerce to effectively seal off an important mineral resource.

Reclamation of the site with vegetation has long been considered a viable option. With the exception of the present study and the field trials of 1975, however, the only other known studies to have investigated the properties of the tailings in terms of their plant growth potential, were small-scale glasshouse trials conducted at Massey University in 1992 and 1996. The first of these studies investigated the growth of radish (*Raphanus sativus*) on Tui tailings treated with varying rates of lime, whereas the second trial investigated the potential of revegetating the tailings with a species of *Thlaspi* known to hyperaccumulate zinc. Satisfactory plant cover was achieved in both trials providing high rates of lime were used to amend the tailings extremely low pH.



Plate 3.3 Surface erosion of Tui tailings embankment following intense rainfall (August 1993).



Plate 3.4 View of the front (western) face of the Tui tailings dam which is covered with a 15-20 cm layer of crushed sulphide-bearing quartz (August 1993).

As later discussed in section 3.7, it is recognised that the establishment of vegetation directly on the tailings may do little to prevent the generation of AMD from the tailings. It is perceived, however, that direct vegetation of the tailings may be a cost effective method of reducing the negative visual impact of the tailings dam and may ultimately inhibit the oxidation of sulphide minerals in and below the root zone of the tailings and thus curb AMD.

Pang (1992) made some tentative suggestions on how to reclaim the tailings dam to prevent AMD. It was suggested that AMD could be controlled by reducing the ground water level in the tailings and by capping the surface of the dam with a combined clay and soil cover. Although the idea of capping the tailings dam is sound, the logic that covering the tailings with a compacted 1 m clay cap may be a “*very economic*” means of preventing AMD is clearly flawed. Such a cover would require the purchase and transportation of an estimated 162,000 m³ of clay to the site. Pang further suggests that if “*rehabilitation*” of the site is required, the clay cap should be covered with a sand drainage layer and 2 m of topsoil sown with metal-tolerant plant species. Why the use of metal-tolerant plant species is advocated on the proposed cover is unclear, as such a cover would clearly host a large variety of both native and exotic plants. The construction of the proposed cover would obviously be extremely costly and superfluous to needs. It is estimated that the purchase of the topsoil alone (excluding transportation costs) would exceed \$3 million (based on conservation price of \$10/m³ and a surface area of 1.62 ha).

Pang’s (1992) suggestion that an essential means of controlling leachates from the dam would be to “*create and maintain an unsaturated zone for the tailings deposits by lowering the ground water table*” is also somewhat flawed. Whilst the reduction of groundwater levels in the dam would serve to further stabilise the tailings, this action may potentially expose more sulphide minerals to oxidising conditions and could in fact increase the contaminant load of drainage waters that would inevitably find their way through the proposed ‘dewatering’ system. As discussed in section 3.6.1 maintaining a water cover is a potentially very useful means of inhibiting the formation of AMD.

Based on the numerous problems associated with the Tui mine site and the anticipated cost of reclaiming the site, it becomes apparent why environmentalists and anti-mining groups alike continually cite Tui as a worst-case mining scenario and as a reason why further hardrock gold/metal mining should not be conducted in Coromandel. Others, however, believe that the reputation of the Tui mine site far outweighs its size and impact on the environment and that much of the anti-mining sentiment in the Coromandel is unjust in that modern-day hardrock goldmining operations are incomparable to that conducted at the Tui Mine during the 1960's and 1970's and that current mining regulations are effective. One thing that is certain is that until the site is 'successfully reclaimed' it will continue to kindle many a heated debate on the pros and cons of the mining industry in New Zealand.

3.3 Sulphide Oxidation & Acid Generation

One factor that is common to many of the highly degraded mining sites found throughout the world is the acidification of sulphide bearing mine wastes and the associated production of metal contaminated mine drainages (Ritcey, 1989). Although sulphide oxidation and the production of metal contaminated drainage have traditionally been associated with the coal mining industry, these processes can potentially impact any site where large volumes of sulphide-bearing materials are exposed to the atmosphere (Skousen, 1995).

Problems arising from sulphide oxidation are also encountered in areas which host acid sulphate soils (Dent, 1986). The natural occurrence of high concentrations of pyrite within the profile of these soils renders them susceptible to acidification when artificially drained or during periods of drought. Acidification occurs when oxygen diffuses into the normally anaerobic subsoil, resulting in the oxidation of pyrite and the concurrent production of acid. Acid sulphate soils are characterised by low pH, nutrient deficiencies, low base status and high salinity and elevated soluble sulphate, Al, Fe and Mn concentrations (Dent, 1986). Physical problems associated with these soils include water stress resulting from the inhibition of root development and poor drainage due to the precipitation of colloidal Fe^{3+} oxides (ochre) in pore spaces and subsurface drains (Dent, 1986). After an extended period of drought, drainage flushed from acid sulphate soils is characteristically very acidic (pH 3.2 to 3.8) and loaded with dissolved

sulphates, Fe^{2+} and Al^{3+} . Large volumes of this drainage can seriously impact the aquatic environment and in extreme cases result in wholesale annihilation of fresh water fish populations (Creagh, 1992).

In order to effectively manage wastes from geological material containing sulphide minerals it is important to understand the reactions that influence acid generation. A substantial amount of research has been published relating to the processes and consequences of pyrite oxidation and methods of controlling it (Singer & Stumm, 1970; Caruccio *et al.*, 1977; Stumm & Morgan, 1981; Costigan *et al.*, 1981; Sullivan & Yelton, 1988, Ritcey, 1989). Useful reviews on AMD control and treatment are also included in Sengupta (1993) and Skousen & Ziemkiewicz (1995). Although much of the research outlined in this literature is focused on the coal mining industry, many of the findings can be directly applied to the reclamation of hardrock gold and base-metal mine sites such as Tui.

It is important to note that not all hazardous drainages emanating from mine sites exhibit acid pH. Many drainage waters including those emanating from the Tui mine adits contain alkalinity predominantly in the form of dissolved carbonate (CO_3^{2-}) or bicarbonate (HCO_3^-). The presence of alkalinity does not preclude the water containing mineral acidity in the form of dissolved ferrous iron (Fe^{2+}) and manganese (Mn^{2+}). Some initially alkaline drainages that contain very high concentrations of these metals are net acid producers. Such drainages can seriously impact the aquatic environment via direct metal toxicity and/or as they acidify due to the oxidation and hydrolysis of dissolved metal cations (Hedin *et al.*, 1994).

Base-metals, including Cu, Pb and Zn commonly occur as sulphide deposits. These deposits are usually poly-sulphidic and contain appreciable quantities of two or more heavy metals that may or may not be of economic significance. Metalloids such as arsenic (As) and antimony (Sb) are found in some sulphide deposits as substituted ions in minerals such as arsenopyrite (FeAsS). Mining wastes originating from poly-sulphidic ore are often particularly difficult to reclaim. Acidification and dissolution of heavy metal-bearing minerals resulting from sulphide oxidation tend to severely inhibit

plant growth and contaminate surface and ground water with these potentially toxic metals.

The AGP and reactivity of sulphide minerals varies considerably and relates to several factors, including galvanic interactions and the crystal structure and composition of the mineral (Kwong, 1995). Not all sulphide minerals, however, oxidise to produce acid. The oxidation of bornite (Cu_5FeS_4) for example, results in the net consumption of acid and other non-ferrous sulphides, such as galena (PbS) and sphalerite (ZnS), undergo oxidation without either producing or consuming acid⁴ (Bruynesteyn & Hackl, 1982; Kwong, 1995). Several iron-bearing sulphide minerals such as pyrite, pyrrhotite, marcasite and chalcopyrite do, however, have the potential to liberate appreciable quantities of acid. Of these minerals pyrite (FeS_2) is the most ubiquitous sulphide mineral and is usually the primary source of acidity in mine spoils and AMD (Arora *et al.*, 1979). This unstable, high energy compound is the most abundant sulphide mineral in the Tui tailings.

3.3.1 Pyrite Oxidation

It is widely accepted that, in an oxidising environment, pyrite reacts with oxygen and water to form a series of soluble hydrous Fe and metal sulphates that may in turn hydrolyse to produce highly acidic Fe^{2+} and sulphate enriched drainages. Subsequent oxidation of Fe^{2+} to Fe^{3+} and its complexation with water forms additional acidity and a series of ferrous and ferric oxy-hydroxides (Caruccio *et al.*, 1988). The oxidation of pyrite is a complex process which includes several types of oxidation-reduction reactions, hydrolysis, complex ion formation, solubility controls and kinetic effects (Nordstrom, 1982). Singer & Stumm (1970) interpret the oxidation of pyrite as an electrochemical corrosion reaction where the reduction of H^+ , H_2O or O_2 is accompanied by the oxidation of pyrite.

⁴ See discussion in section 3.3.2.

The overall oxidation reaction of pyrite is exothermic and is often summarised by reaction (1) below. This incongruent equation indicates that the ultimate products of the oxidation of pyrite are sulphuric acid and ferrihydrite (Backes *et al.*, 1986). Ferrihydrite or ferric oxy-hydroxide is a highly insoluble, amorphous iron hydroxide gel that is often referred to as ochre or 'yellow boy' (Tucker *et al.*, 1987). It forms from the hydrolysis of Fe^{3+} and is a tell-tale sign of AMD when found lining stream or river beds. Reaction (1) indicates that under ideal conditions each mole of pyrite will oxidise to liberate 1 mole of ferrihydrite and 2 moles of acid.



This overall equation simplifies the oxidation of pyrite, however, which in reality is not a simple one-step reaction but a series of generally aerobic reactions involving a number of intermediates (Backes *et al.*, 1986). Once initiated, the reactions that oxidise pyrite and result in the net production of acid are believed to develop syngenetic interactions that accelerate the oxidation process (Chamber of Mines of South Africa, 1981; Caruccio *et al.*, 1988). These reactions are summarised below (Stumm & Morgan, 1980).



Reactions (2) and (5) indicate that pyrite is initially oxidised by oxygen and then by Fe^{3+} . The oxidation of pyrite is initiated in reaction (2) where oxygen is seen to react with pyrite to release Fe^{2+} . This reaction is purely chemical and highly dependent on pH, taking place only at an appreciable rate above pH 5 (Singer & Stumm, 1970).

The overall rate of pyrite oxidation is relatively slow above pH 3.5 because the majority of ferric ions (Fe^{3+}) are removed from solution as the result of $\text{Fe}(\text{OH})_3$ precipitation (reaction 4). The formation of ferrihydrite renders the Fe^{3+} unavailable for direct oxidation of pyrite, a reaction which occurs at a much faster rate than pyrite oxidation

which involves oxygen only (Dent, 1986). As the acidity of the system increases, however, Fe^{3+} become increasingly soluble and begins to act as an oxidising agent (reaction 5). Below pH 3.0, the majority of Fe^{3+} are dissociated from water and are available to rapidly oxidise pyrite (Nordstrom, 1982). This reaction readily proceeds under anoxic conditions and can lead to the acidification of sealed pyritic spoils (Wiggering, 1993).

Whereas the ultimate driving force of pyrite oxidation is atmospheric oxygen, the fundamental mechanism and the major rate determining step is not thought to involve oxygen at all (Nordstrom, 1982). The oxidation of Fe^{2+} to Fe^{3+} as described in reaction (3) is widely believed to be the rate limiting step in the oxidation of pyrite. This is due to pyrite being able to reduce Fe^{3+} to Fe^{2+} faster than Fe^{2+} can be regenerated to Fe^{3+} by oxygen (Nordstrom, 1982). In nature, reaction (3) is usually catalysed by the bacterium *Thiobacillus ferrooxidans*, which can dramatically increase the overall oxidation rate of pyrite (Zajic, 1969). *T.ferrooxidans* is estimated to increase the oxidation rate of Fe^{2+} by 5 to 6 orders of magnitude, making the oxidation rate of Fe^{2+} in the presence of this bacterium, comparable to, or slightly higher than the pyrite oxidation rate by Fe^{3+} (Lacey & Lawson, 1970; Singer & Stumm, 1970; Nordstrom, 1982). Where the pH of the material has been amended to between 6 and 7, however, the abiotic oxidation of Fe^{2+} , although slow, will be the dominant oxidation pathway and the diffusion of atmospheric oxygen into material will determine the rate of reaction (Van Breeman, 1973; Backes *et al.*, 1986; Caruccio *et al.*, 1988).

The bacterial catalysis of reaction (3) is extremely important in that it initiates a cyclical system in which Fe^{2+} ions released from the initiator reaction (reaction 2) are oxidised to Fe^{3+} ions which then oxidise pyrite (reaction 5) to liberate more Fe^{2+} ions (Singer & Stumm, 1970; Backes *et al.*, 1986). Research suggests that iron-oxidising bacterial populations are responsible for about $\frac{1}{2}$ to $\frac{3}{4}$ of the acid produced during pyrite oxidation (Zajic, 1968; Caruccio *et al.*, 1988).

Whilst a variety of bacteria are known to play a role in the biochemical oxidation of sulphide minerals, the acidophilic bacterium *Thiobacillus ferrooxidans* is considered to be by far the most important organism involved (Ritcey, 1989; Ehrlich, 1995).

T.ferrooxidans is classified as a chemo-autotrophic bacteria due to its ability to aerobically oxidise Fe^{2+} and sulphur compounds as a sole source of energy for growth and carbon dioxide fixation (Zajic, 1969; Brown *et al.* 1990). Although the bacterium obtains its oxygen and carbon dioxide from the air, it requires an aquatic environment, ammonia and small quantities of phosphate, calcium and magnesium for growth.

The ability of *T.ferrooxidans* to oxidise many other sulphide minerals including chalcopyrite, sphalerite galena, millerite and molybdenite, has resulted in its widespread use in the commercial bioleaching and biobenefaction of low-grade sulphidic ores (Zajic, 1968; Ehrlich, 1995). Optimum pH levels for the growth of *T.ferrooxidans* and hence the catalytic oxidation of sulphide minerals are between 2.4 and 3.6 (Caruccio *et al.*, 1988). Below pH 2.0 and above pH 3.6 biotic pyrite oxidation rates decrease dramatically as either the bacterial population is displaced and/or the solubility of Fe^{3+} decreases (Dent, 1986). Ritcey (1989) suggests that the optimum temperature for growth of *T.ferrooxidans* is between 35 and 45°C.

To summarise, acid generation is generally most severe in highly pyritic materials where the acid produced can quickly neutralise carbonates, overcome pH buffering systems and lower the pH sufficiently to solubilise Fe^{3+} and promote the activity of iron-oxidising bacteria (chiefly *Thiobacilli* spp.) which in turn accelerate the oxidation of pyrite by Fe^{3+} (Backes *et al.*, 1986). Maintaining the pH of an acid generating material above pH 4.0 is believed to substantially reduce its ability to produce acid as the activity of *Thiobacilli* is greatly reduced and Fe^{3+} becomes insoluble and unavailable to oxidise pyrite. Although acid is produced in reactions (2), (4) and (5), the majority of acid forms as a result of the hydrolysis of soluble hydrous metal sulphates formed during the oxidation reactions (reaction 5). Further acid is produced as Fe^{3+} complexes with water to form ferrihydrite or ferric oxy-hydroxide (reaction 4) (Caruccio *et al.*, 1988).

3.3.2 Sulphide Oxidation *in situ*

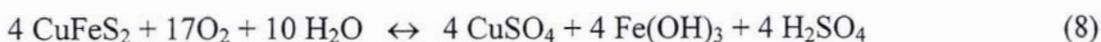
The above discussion is somewhat simplified in that reactions (1) to (5) assume that complete hydrolysis of Fe^{3+} occurs, resulting in the net production of 2 moles of sulphuric acid per mole of pyrite. In an acidic environment, however, complete hydrolysis of the Fe^{3+} is unlikely to occur and the amount of acid generated in the field

situation is likely to be significantly less. Bruynesteyn & Hackl (1982) suggest that Fe is likely to be precipitated as basic ferric sulphate or as jarosite-type minerals⁵.

If it is assumed that all Fe is precipitated as hydronium-jarosite $[\text{H}_3\text{O}.\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]$, Bruynesteyn & Hackl (1982) suggest that the oxidation of pyrite would be better summarised by reaction (6) below.



In this reaction every mole of pyrite is oxidised to produce 1.33 moles of sulphuric acid. Bruynesteyn & Hackl (1982) believe that, in a natural situation, the amount of acid produced will depend upon a combination of equations (1) and (6) and will thus vary between 1.33 and 2.0 moles of sulphuric acid per mole of pyrite. Similarly, the oxidation of 1.0 mole of chalcopyrite is thought to produce between 0.33 and 1.0 mole of acid (reactions 7 & 8 respectively). Although jarosite weathering via hydrolysis will generate acidity research outlined by Sobek *et al.* (1987) found that the effective acidity produced from jarosite hydrolysis is not large compared to that produced by pyrite oxidation (Sobek *et al.*, 1987)



As previously mentioned, other non-ferrous sulphides, such as galena and sphalerite undergo oxidation. Acid, however, is neither produced nor consumed and the reaction can be represented by reaction (9). Although acid is not produced by the oxidative dissolution of these minerals, the resulting sulphate salts have an acidic pH which may mobilise the metals that they contain (Bruynesteyn & Hackl, 1982). Dissolved sulphate, Pb^{2+} and Zn^{2+} liberated during the reaction can contaminate the soil solution and

⁵ $\text{A}.\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ where A can equal H_3O^+ , NH_4^+ , K^+ , Na^+ etc. Jarosite commonly occurs as earthy filling of voids or as mottles in the soil matrix and is only formed in acidic (pH 2 to 4), oxidising ($\text{Eh} > 400 \text{ mV}$) environments (Sobek *et al.*, 1987). From a plant growth perspective the formation of potassium jarosite $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$ is significant in that it tends to precipitate K and thus reduce the availability of this macronutrient to plants (Barnhisel *et al.*, 1982).

drainage waters. Fortunately the mobility of Pb^{2+} is comparatively very low due to its tendency to react with sulphate to form highly insoluble anglesite (PbSO_4) under oxidising conditions.



Pyrite is thus seen to be the most significant source of acid and can theoretically produce as much as 2 moles of acid per 1 mole of pyrite. The amount of acid generated in reality, however, is likely to be significantly less due to incomplete sulphur oxidation.

A variety of oxidation products can potentially form in pyrite-bearing materials ranging from insoluble iron hydroxides such as ferrihydrite [$\text{Fe}(\text{OH})_3$] to highly soluble iron sulphate hydrates including, melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) and szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) (Nordstrom, 1982). The more soluble sulphates generally form during dry periods (evapotranspiration > rainfall) which invoke capillary rise, the subsequent concentration of ions and the precipitation of efflorescent salts (Nordstrom, 1982; Sobek *et al.*, 1987). Goethite (FeOOH) and haematite (Fe_2O_3) in contrast are the most stable of the oxidation products and form from the dehydration of ferrihydrite and/or jarosite-type minerals.

3.3.3 Factors Affecting Sulphide Oxidation Rates

As alluded to in the previous discussion, there are a multitude of factors that affect the reaction rate of sulphide minerals. These include; *crystal structure* and *adsorbed impurities* (Pugh *et al.*, 1984; Caruccio *et al.*, 1988, 1995; Keller & Murr, 1982; Kwong, 1995), *surface area* (Singer & Stumm, 1970; Caruccio, 1973; Pugh *et al.*, 1984; Arora *et al.*, 1979), *temperature* (Caruccio *et al.*, 1988; Scharer *et al.*, 1995), *oxygen concentrations* (Pugh *et al.*, 1984; Erickson *et al.*, 1985; Wiggering, 1993; Scharer *et al.*, 1995; Lin, 1997), *water partial pressure* (Caruccio *et al.*, 1988), *solution pH* (Costigan *et al.*, 1984; Gemmell, 1981; Backes *et al.*, 1986), *flushing frequencies* (Geidel, 1979; Caruccio *et al.*, 1988), *galvanic interactions* (Natarajan, 1990; Tuovinen, 1990; Kwong, 1995) *iron-oxidising bacteria* (Zajic, 1969; Brown *et al.*, 1990; Ehrlich, 1995) and *inhibitors* (Baldi & Olson, 1987; Ritcey, 1989) and of course *time*. Caruccio *et al.* (1988) provide a useful review of the various factors governing the oxidation rate

of pyrite with an emphasis on the role of this mineral in the production of acid from colliery spoils.

3.4 Acid Mine Drainage

Based upon the preceding discussion it is evident that solution pH is one of the most important factors controlling the rate of sulphide oxidation as it not only governs the solubility/availability of Fe^{3+} but also the activity of iron-oxidising bacteria responsible for the biocatalysis of sulphide minerals. The presence of reactive (acid generating) sulphides, iron-oxidising bacteria, water and oxygen and low concentrations of acid neutralising carbonate minerals can ultimately lead to the release of acid mine drainage (AMD) which is a solution characterised by low pH and high concentrations of sulphate, Fe and other metals (Caruccio, 1975). Some researcher define AMD even further as ‘...water with a pH below 2.3, anion concentrations exceeding 10,000 mg/l and acidities averaging 5,000 mg/l as CaCO_3 ’ (Caruccio *et al.*, 1981 cited in Tucker *et al.*, 1987).

Acidity in AMD is comprised of *hydrogen ion acidity* (a measure of free H^+ ions), *organic acidity* associated with dissolved organic compounds and *mineral acidity* which arises from the presence of dissolved metals commonly Al, Fe and Mn in the water (Hedin *et al.*, 1994). These metals generally account for most of the mineral acidity found in coal spoil, however, drainage from base-metal mines such as the Tui Mine, typically contains significant amounts of Cd, Cu, Pb and Zn which can contribute significantly to mineral acidity (Pang, 1992; Skousen, 1995).

The drainage quality of water emanating from sulphide bearing material is largely dependent on the ratio of pyrite to carbonate. In general, sulphide rich and carbonate poor materials are expected to produce acidic drainage if exposed to oxidising conditions (Skousen, 1995). The presence or absence of calcareous material in pyrite-bearing strata is thus generally regarded as the most critical element in determining drainage quality (Caruccio *et al.*, 1988). The pH of the effluent produced from the waste materials plays an important role in solution quality. Not only does the pH control the solubility of the various metals but in the case of the sulphide wastes, a low pH encourages biological breakdown of metal sulphides, thus increasing the rate of

solubilisation of corresponding metal sulphides as well as production of ferric sulphate lixiviant (Bruynesteyn & Hackl, 1982).

In the case of acid sulphate soils, while most of the Fe mobilised by the oxidation of pyrite remains in the soil profile only a small fraction of the sulphate is retained, usually as jarosite or as basic Al sulphate (Dent, 1986). Most soluble sulphur is lost to drainage although some diffuses down to the reduced substratum where it may re-precipitated as sulphides (Dent, 1986). Gypsum and soluble sulphates often accumulate at locations where evapotranspiration exceeds rainfall (Sobek *et al.*, 1987).

The concentration of metals and metalloids in mine drainages depends on a multitude of factors including Eh, pH, water composition (eg. high Fe^{3+} levels may result in co-precipitation and/or adsorption of heavy metals), flow rates, sediment grain-size and the type and extent of mining operations (Livingston, 1987). Highly toxic AMDs are often generated from base metal mines containing metals and metalloids such as As, Cd, Cu, Hg and Pb. These potentially toxic metals may be liberated into the aquatic system and food chain as a result of sulphide oxidation, acidification and dissolution processes occurring in host materials.

Whilst it is beyond the scope of this study to further review the production, geochemistry and impact of AMD, it must be stressed that it is a widespread phenomenon that affects numerous active and abandoned mine sites around the world. In the US alone it is estimated that AMD adversely affects over 6,500 km of rivers and streams and 730 km² of lakes and reserves (Kleinmann, 1991). Sites impacted by AMD are found in a diverse range of countries including *Wales* (Fuge *et al.*, 1991), *England* (Davies & Ballinger, 1990), *Spain* (Perez & Calvo de Anta, 1992), *Greece* (Kelepertsis & Bibou, 1991), *USA* (Kleinmann, 1991; Skousen, 1995) *Canada* (Ritcey, 1989), *Australia* (Harries & Ritchie, 1988; Bell *et al.*, 1989) and of course *New Zealand* (Tay, 1980; Hendy, 1981; Pang, 1992, 1995). A variety of useful literature pertaining to AMD exists (Singer & Stumm, 1970; Helz *et al.*, 1987; Ritcey, 1989; Skousen *et al.*, 1990; Kleinmann, 1991; Sengupta, 1993; Skousen & Ziemkiewicz, 1995).

3.4.1 Acid Mine Drainage Prediction

Several approaches have been developed to predict mine drainage quality including:- (i) comparison with neighbouring mines, (ii) geological and paleoenvironmental mapping, (iii) geochemical static tests, (iv) geochemical kinetic tests and (v) mathematical modelling (Ritcey, 1989; Sengupta, 1993). Whilst all of these methods are potentially useful, the following review focuses on the two most commonly used methods of assessing the Net Acid Generating Potential (NAGP) and liming requirements of sulphide-bearing mine wastes in Australasia (Acid Base Accounting and Hydrogen Peroxide Oxidation). A cursory discussion of alternative kinetic tests is given.

3.4.1.1 Acid Base Accounting (ABA)

Acid base accounting is a static test that provides a theoretical estimate of the NAGP of a geological material, based on the difference between the acid-forming and acid-neutralising capacities of the material (Sobek *et al.*, 1987; Miller *et al.*, 1994). ABA was the first technology available to assess the chemical quality of *in situ* overburden. This prompted the development of pre-mine planning for reclamation and selective handling procedures of acid generating material, practices which are now commonplace and usually required by law (Skousen *et al.*, 1995).

(i) The Development of ABA

The ideas that initiated the development of ABA originated from research conducted in the early twentieth century investigating the composition and relative reactivity of elemental compounds in the Earth's crust (Skousen *et al.*, 1995). The method was chiefly pioneered and trialed in the coal fields of eastern USA, with reports acknowledging the effects of spoil quality on plant growth dating back to the 1940's (Skousen *et al.*, 1995).

Early ABA systems focused on the categorisation of mine spoil into classes based on rock composition and acidity. Knabe (1964) was amongst the first researchers to document the importance of the relative proportions of acid to non-acid generating minerals in mine spoil. He developed a method called a 'base-acid balance' which estimated the theoretical quantity of acidity or alkalinity that a mine spoil could produce upon weathering (Skousen *et al.*, 1995). The early methods, although useful for

determining lime and fertiliser application requirements and selecting suitable plant species for revegetation purposes, fell short of being able to accurately estimate the potential of undisturbed overburden to generate acid (Skousen *et al.*, 1995). Thus, suitable, non-acid generating material was not always accessible for revegetation purposes because spoil management couldn't be accurately planned prior to mining.

Much of the subsequent ABA research was conducted by researchers at West Virginia University, where a system for balancing the acid and alkaline production potential of *in situ* overburdens was developed (Smith *et al.*, 1974; Smith & Sobek, 1978; Sobek *et al.*, 1978). Soon after the development of such a system, practitioners began to log sulphur profiles and the acid-neutralising capacities of materials in stratigraphic sections overlaying coal seams prior to mining. This enabled the net acidity or alkalinity for each geologic unit to be calculated and an estimate of the material's NAGP to be made (Skousen *et al.*, 1995). Whilst a variety of factors are known to influence the acid producing potential of geological materials, ABA was developed on the premise that the mineral composition of a material largely dictates its NAGP (Skousen *et al.*, 1995).

(ii) ABA Methodology

The ABA procedure firstly involves estimating the Acid Generating Potential (AGP)⁶ of a material. For coal overburden this is usually done by determining the sulphidic sulphur content of a material. The AGP of a material is then estimated stoichiometrically by assuming that two moles of CaCO₃ will be required to neutralise the acidity potentially produced from the oxidation of 1.0 mole of pyrite as per reactions (1) and (2).



Based on the stoichiometry of reaction (2) it holds that each mole of pyrite contains 2 moles of sulphur which if oxidised will require 2 moles of CaCO₃ to neutralise it. Using the molecular weights of sulphur (≈ 32) and calcium carbonate (≈ 100) it is possible to calculate the theoretical quantity of CaCO₃ required to neutralise the acidity produced

⁶ Also commonly referred to as Maximum Potential Acidity (MPA) or Acid Producing Potential (APP).

from 1000 Mg of material containing 0.1% (1000 kg) of sulphidic sulphur (S_s) as follows;

$$\begin{aligned}
 \text{Since } 32 \text{ g } S_s &\cong 100 \text{ g } CaCO_3 \\
 \therefore 1000 \text{ kg } S_s &\cong (100/32) * 1000 \text{ CaCO}_3 \\
 &\cong 3125 \text{ kg } CaCO_3
 \end{aligned}$$

The material's AGP is generally presented as calcium carbonate equivalents [Mg $CaCO_3$ /1000 Mg material]. Based on the stoichiometry of the oxidation of pyrite and its reaction with calcium carbonate, 1000 Mg of material containing 0.1% sulphur (all as pyrite) theoretically yields an amount of sulphuric acid that would require 3.125 Mg of $CaCO_3$ to neutralise it (Smith *et al.*, 1974; Skousen *et al.*, 1995).

The second stage of the ABA method involves determining the material's neutralising potential (NP). The base content of a material (commonly present as carbonates or exchangeable cations on clays) significantly influences the material's AGP (Smith & Sobek, 1978; Geidel, 1979; Skousen *et al.*, 1995). In a material containing alkaline components and pyrite the soluble bases must generally be sufficiently active to neutralise the acid at a rate equal to or exceeding the rate of acid production to prevent the material's acidification under oxidising conditions (Skousen *et al.*, 1995).

The most common means of assessing a material's acid neutralising potential (Neutralisation Potential, NP) is to chemically digest a pulverised sample in an acidic solution of known concentration (0.10M HCl is often used). The solution is then back-titrated to a predetermined endpoint with a standard base (NaOH) to determine the amount of acid consumed by the material. The base account is calculated from the weight of sample digested, the volume and normality of the acid and the amount of titrant used (Sobek *et al.*, 1978). The NP of a material is again converted to calcium carbonate equivalents.

Using ABA the NAGP of a material (and thus the quality of drainage likely to emanate from the material) is predicted by subtracting the material's AGP from the material's NP after conversion to $CaCO_3$ equivalents. A negative NAGP value indicates that the material is capable of producing acid mine drainage, whereas a positive value

conversely indicates that the material is likely to produce circumneutral or alkaline drainage (Evans & Skousen, 1995).

(iii) Limitations of ABA

The major limitations associated with traditional ABA are that:- (i) all sulphur is generally assumed to be present as pyrite, (ii) it is assumed that all of the acid consuming minerals are available for acid neutralisation, (iii) results are difficult to interpret if AGP and NP are near or in balance and (iv) the reaction kinetics of the system are not considered (Miller & Murray, 1988; Ritcey, 1989).

Since ABA has largely been developed by the coal mining industry for the assessment of colliery spoil, it is based on the assumption that all acidity originates from the oxidation of pyrite (Skousen *et al.*, 1995). Although this assumption may hold true for the majority of colliery spoils, it may overestimate the AGP of materials containing appreciable amounts of non-acid generating sulphide minerals, particularly if the AGP of the material is estimated from sulphur analysis of the material. Overestimation is likely to stem from the inability of standard sequential sulphur extractions to adequately differentiate between acid generating and non-acid generating sulphide sulphur.

The pyrite content of polysulphidic materials may therefore be better predicted by determining pyritic Fe content. Allowances must, however, be made for materials containing substantial quantities of non-pyritic but acid generating minerals such as covellite (CuS) or chalcopyrite (CuFeS₂). Determination of pyritic Fe alone would fail to take into account the acidity that oxidation of these sulphide minerals would generate.

It was thus postulated that without significant modification, traditional ABA methods would overestimate the AGP of the Tui mine tailings due to the occurrence of relatively high concentrations of sulphide minerals such as galena (PbS) and sphalerite (ZnS) which are considered to be non-acid generating (Bruynesteyn & Hackl, 1982; Kwong, 1995).

Research by Cravotta *et al.*, (1990) and Brady *et al.*, (1994), however, suggests that traditional ABA methods may in fact substantially underestimate the liming

requirements of acid generating materials. The standard ABA method outlined above presumes 2 moles of H^+ may be neutralised by 1 mole of $CaCO_3$. The stoichiometry of this reaction thus assumes that all CO_2 will exsolve. In reality, however, some CO_2 will dissolve forming a weak acid that reacts with carbonate minerals. Assuming no exsolution of CO_2 , 1 mole of FeS_2 will produce 4 moles of H^+ , which may be neutralised by 4 moles of $CaCO_3$. On a weight basis, 1 g of pyritic sulfur will thus be neutralised by 6.25 g of $CaCO_3$. Considering this equivalent weight, the AGP as $CaCO_3$ deficiency per 1,000 Mg of overburden should be computed by multiplying total sulfur, in weight percent by 62.5 instead of the factor that has been previously used (31.25). Cravotta *et al.*, (1990) concede that actual acidity may be less than the computed AGP because not all CO_2 dissolves and not all sulfur generates acidity.

The methods commonly used to assess the NP of mine wastes have also drawn some criticism in recent years. Lapakko (1994) suggests that digestion methods used to assess NP of wastes may overestimate the NP present as calcium carbonate and magnesium carbonate. The overestimation is attributed to the fact that whilst at low pH (during the digestion) the dissolution of acid consuming minerals (eg. plagioclase, pyroxene and olivine) present in the host rock neutralise acid, under field conditions the rate of acid neutralisation by such minerals is often too slow to neutralise generated acid. The presence of high concentrations of siderite ($FeCO_3$) may further contribute to excessive NP estimates due to inadequate quantification of Fe^{2+} acidity. Errors in NP estimation may result in the erroneous classification of acid generating material as non acid-generating (Lapakko, 1994).

Despite the apparent simplicity of ABA this method cannot be used to definitively predict the quality of drainage emanating from mine wastes at any given time in the future. Acid generating processes and thus the production of acid mine drainage are time-dependent and are functions of numerous interactive factors such as mineralogy, grain-size, site hydrology and climate. For this reason ABA can only be used as a qualitative prediction method to indicate whether or not materials have the potential to generate net acidity in the future (Sengupta, 1993). ABA does, however, provide a useful guide for estimating the liming requirements of acid generating materials where

pH amendment is the intended means of controlling the generation of acid mine drainage.

3.4.1.2 Hydrogen Peroxide Oxidation (HPO)

The ability of hydrogen peroxide (H_2O_2) to rapidly oxidise pyritic material has long been recognised and several procedures to determine the potential acidity of pyritic material are based on this reaction (Sobek *et al.*, 1978; O'Shay *et al.*, 1990; Finkelman & Giffin, 1986; Finkelman, 1987; Miller *et al.*, 1994). Although several HPO methods have been devised, they are all basically variations of one another, with many of the more recent variants being based largely on the method of Smith *et al.* (1974).

(i) HPO Methodology

The principal of these methods is to use H_2O_2 to rapidly oxidise pyrite which results in the subsequent production and liberation of hydrogen ions (H^+) and metal sulphates into solution. A semi-quantitative estimate of the AGP of the material can then be made by quantifying either the titratable acidity or the amount of sulphate (SO_4^{2-}) produced during the oxidation reaction.

Qualitative HPO methods also exist and are commonly applied in the field as a means of rapidly assessing the ability of a material to produce acidity. Although the exact procedures of these qualitative tests tend to vary widely, they basically involve the oxidation of a set amount of material with a specific volume of dilute H_2O_2 . The oxidation of the pyrite results in the liberation of H^+ and their concentration is measured indirectly using a standard soil pH meter. The degree of acidification (pH) indicates the material's ability to produce acid. Many of the methods use an arbitrary solution value of $\text{pH} \leq 3.0$ to indicate if the material is likely to acidify and potentially generate AMD (Blakemore *et al.*, 1987).

(ii) Limitations of HPO Methods

Several previous studies have indicated that the HPO methods used for predication of AGP of colliery spoils are unreliable (Dacey & Colbourne, 1979; Sobek *et al.*, 1987; Caruccio *et al.*, 1988). Research reported by Dacey & Colbourne (1979) assessed six methods for the determination of iron pyrites in coal mine spoil, including one HPO

method that quantified $\text{SO}_4^{=}$ liberation. One of the disadvantages recognised with the HPO method studied was that when it was used to assess spoils containing carbonate minerals, erroneously low pyrite content determinations were made. Even when the samples were pre-treated with HCl to prevent the catalytic decomposition of H_2O_2 by carbonates, considerable scatter in the results was found. Although the method was found to be capable of distinguishing between samples of low, medium and high pyrite content it was not considered to be reliable (Dacey & Colbourne, 1979).

More recently, a comparative study was made between Acid-Base Accounting and HPO prediction methods (Ammons & Shelton, 1988). In this study nearly one hundred samples of overburden of varying sulphur content (0.006-1.328 %) were analysed to compare these procedures. Results indicated that for unweathered samples there was a positive correlation between the two methods, however, the relationship was found to be less pronounced for weathered overburden samples. The coefficients of determination (r^2) for the unweathered and weathered samples were 0.89 and 0.71 respectively. The authors suggested that the HPO procedure was best used to predict the NAGP of fresh, unweathered samples (Ammons & Shelton, 1988).

Caruccio *et al.* (1988) also report that HPO methods tend to give highly variable results and may grossly overestimate the potential acidity of samples high in organic sulphur. Sobek *et al.* (1987) suggest that HPO methods can be used successfully in some overburden samples providing the unit mineralogy is “simple”, unstabilised H_2O_2 is used and excess H_2O_2 is destroyed prior to titration. The authors did not recommend the procedure for the routine analysis of all overburden. Finkelman & Giffin (1986) similarly reported that the use of H_2O_2 to rapidly oxidise pyrite has met with “*decidedly mixed results*”.

(iii) Application of HPO Methods

Despite the fact that there is much debate about the ability of HPO methods to accurately predict the AGP of pyritic material, development of the method is continuing. An HPO method is currently being used to identify potentially acid forming materials at mine sites in Australia, New Zealand, Papua New Guinea and Indonesia (Miller *et al.*, 1994). Research is being conducted to evaluate this same method to see if the kinetics of acid

generation and neutralisation can be predicted. The potential of HPO methods to indicate pyrite activity was recognised in earlier research (Dacey & Colbourne, 1979; Finkelman & Giffin, 1986). Preliminary investigations by Miller *et al.* (1994) indicate that a relationship may exist between the kinetics of the HPO method and the lag period of acid generation observed in the field. The paper suggests that if a relationship is established it may be possible to provide a time factor for use in waste management design (Miller *et al.*, 1994).

Most of the HPO methods developed to date (with the notable exception of that of Miller *et al.*, 1994) have been designed almost exclusively for assessing the AGP of colliery spoil. When used to assess the AGP of poly-sulphidic mine tailings such as the Tui tailings, semi-quantitative HPO methods based on $\text{SO}_4^{=}$ determination may tend to overestimate the material's AGP. These methods assume that all the $\text{SO}_4^{=}$ produced by the oxidation reaction results from the oxidation of pyrite. In the case of poly-sulphidic tailings a significant proportion of the $\text{SO}_4^{=}$ may in fact be produced by the oxidation of non-pyritic sulphides such as galena (PbS) or sphalerite (ZnS). Bruynesteyn & Hackl (1982) and Kwong (1995) report that whilst these non-pyritic minerals undergo biochemical oxidation, acid is neither consumed nor produced during the solubilisation reaction. Therefore in the case of a material which contains appreciable quantities of non-ferrous sulphides, the assumption that all $\text{SO}_4^{=}$ is derived from the oxidation of pyrite is erroneous and will result in the overestimation of the materials pyrite content and thus its AGP.

It is postulated that the HPO method of Miller *et al.* (1994) which is based on the quantification of titratable acidity (as opposed to $\text{SO}_4^{=}$ content) may also overestimate the AGP of poly-sulphidic tailings that contain significant quantities of non-pyritic sulphide minerals. Although these minerals reportedly react with H_2O_2 to release hydrogen ions (Finkelman & Giffin, 1986) their biochemical oxidation does not result in the net production of acid (Bruynesteyn & Hackl, 1982; Kwong, 1995). The extent to which the method of Miller *et al.*, (1994) would overestimate the AGP of poly-sulphidic tailings would clearly depend on the relative proportions of pyritic to non-pyritic sulphides in the material.

3.4.1.3 Alternative Prediction Methods

Over the past few decades a variety of alternative procedures have been developed to characterise mine wastes. Caruccio (1975), for example, discusses the combined use of optical mineralogy and sulphur analysis to predict the reactivity and net acid generating of pyrite bearing mine wastes. Pulford & Duncan (1978) outline a very different method to qualitatively assess the degree of weathering and the reactivity of coal wastes based on plotting pH against acetic acid extractable (0.5 M) sulphate levels.

Kinetic AMD prediction tests differ from the aforementioned static tests in that they involve the weathering of mine material under field or controlled laboratory conditions and are designed to provide information relating to the reaction rates and temporal variation of acid generation. Due to their nature they are run over much longer periods (generally several weeks) and require a greater commitment of resources. They are often used to confirm the findings of static tests and to select and optimise appropriate drainage control techniques based on the predicted severity and likely duration of AMD (Sengupta, 1993; Miller *et al.*, 1994). There are numerous types of kinetic tests; the most commonly encountered are summarised in Table 3.1.

Table 3.1 Kinetic Tests for the Prediction of Acid Mine Drainage
(adapted from Ferguson , 1986 cited in Ritcey, 1989).

Kinetic Test	Principles	References
Soxhlet Reactors	Designed to simulate the weathering of geological material. Uses water or dilute acid to repeatedly leach material in a sealed reaction vessel. Leachates are analysed.	Sullivan & Sobek (1982)
Bacterial Incubations/ Shake Flasks	Sample is placed within reaction vessel and inoculated with <i>Thiobacillus ferrooxidans</i> . Samples incubated for several weeks and leachates are analysed periodically.	Bruynesteyn & Hackl (1982)
Humidity Cells	Sample is placed in a sealed container through which humid air and then water is passed. Leachates are analysed	Caruccio (1977) Sobek <i>et al.</i> (1978) Sullivan & Sobek (1982)
Columns	Material is placed in a column and leached periodically with distilled water to simulate <i>in situ</i> leaching by rainfall. Resulting leachates are analysed.	Sturey <i>et al.</i> (1982)
Test Plots	Bulk sample of mine waste is placed on impervious surface in field. Leached precipitation is collected in a sump and monitored over long term (>1 year).	Eger & Lapakko (1981)

Review of the literature clearly indicates that currently there is no universally accepted approach to predicting the net acid generating potential of sulphide-bearing mine wastes. Sengupta (1993) suggests that accurate prediction of long term drainage quality is only possible through the application of quantitative mathematical models that can reliably extrapolate the results of kinetic tests.

3.4.2 Metal Quantification in Mine Materials

Based on the perceived limitations of most standard static tests it was decided to approach the prediction of the Tui tailings' AGP using a less conventional approach and to compare the results of the devised method (Theoretical AGP) with those obtained using the HPO method of Miller *et al.* (1994). The TAGP method is outlined fully in Chapter 4 (section 4.4) but basically involved the quantification of sulphidic Cu and Fe from which the tailings' chalcopryrite and pyrite content (and ultimately TAGP) was estimated. The TAGP technique is similar in principal to pre-existing methods that have been developed for determining the pyrite content of colliery spoil via Fe analysis⁷.

The TAGP method used in this study required the quantification of two forms of Cu and Fe in the tailings; acid generating (sulphidic) and non-acid generating (non-sulphidic) Cu and Fe. One of the primary objectives born in mind during the selection of suitable extractants for the determination of these fractions was to use extractants that would also provide useful information relating to the 'plant available' and total metal content of the tailings. In addition the speed, simplicity and versatility of the extractants and/or extraction procedures was also considered.

The following literature review was undertaken to identify potentially useful extractants available for the quantification of sulphidic and non-sulphidic metals in the Tui tailings and other mining wastes.

⁷ Discussions of AGP prediction using Fe analysis are included in Burns (1970), Dacey & Colbourne (1979) and Sobek *et al.* (1987).

3.4.2.1 Non-Sulphide Fraction

Although a great number of secondary iron-bearing minerals such as rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$), ferroxahydrite ($\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$) and melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) can potentially form in the Tui tailings as a result of sulphide oxidation, these minerals are highly soluble and thus generally unstable and prone to leaching in acidic conditions. The majority of non-sulphidic iron in the tailings was therefore believed to be associated with relatively insoluble secondary iron phases including amorphous ferrihydrite ($\text{Fe}(\text{OH})_3$), goethite (FeOOH) and sulphates such as jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) which are stable at low pH (Sullivan *et al.*, 1988).

The mobility of non-sulphidic Cu in the tailings was expected to be relatively high due to the lack of both organic matter and high CEC clays. Like many of the hydrated Fe sulphate minerals, the majority of the copper sulphate minerals such as chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), antlerite ($\text{Cu}_3\text{SO}_4(\text{OH})_4$) and brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$) are highly soluble. The primary form of non-sulphidic copper in the tailings was thus predicted to be present as adsorbed Cu^{2+} on hydrous iron/manganese oxides and aluminosilicate gels which are known to scavenge copper and other transition metal ions released from dissolution of sulphides (Ritcey, 1989; Walder & Chavez, 1995).

For the purposes of this study the non-sulphidic fraction of the tailings was considered to broadly correlate to labile Cu and Fe forms in the tailings and was thus considered to be best estimated by using extractants suited to extracting ‘plant available’ (labile) Fe and Cu.

3.4.2.2 Extractants

Although commonly requested by regulatory authorities, total elemental analysis of mining wastes is generally of little use in assessing the potential toxicity of the material to plants and the environment in general (Berg, 1978; Safaya *et al.*, 1987). Plant available trace element concentrations are thus generally estimated using one of what Brooks (1987) describes as a “bewildering” range of soil extraction procedures that have been developed (eg. Lindsay & Norvell, 1969, 1978; Baker & Amacher, 1982; Jopony & Young, 1993, Luo & Rimmer, 1995). Despite being the focus of much research over the past few decades, there is still little consensus as to the extractant and procedure

which should be universally adopted (Brooks, 1987). Bioassay procedures, although generally considered to offer the most reliable data pertaining to the availability of various elements to plants are generally time consuming and expensive (Chadwick, 1973; Brooks, 1987; Luo & Rimmer, 1995).

Many of the commonly employed extraction methods have been developed to detect deficiencies rather than toxicities and are therefore of dubious value when it comes to estimating the bioavailability of 'micronutrients' in mining wastes which may be present in concentrations 1000-fold greater than those found in 'natural' soils (Berg, 1978). Although the complexity of the extractants and procedures varies substantially, the two most commonly used types of soil extractants are weak inorganic acids and chelating agents.

(i) Chelating Agents

The use of a chelating agents as a potential extractant to assess the concentrations of 'non-sulphidic' Cu and Fe and other cations in the Tui mine tailings was carefully considered. Although extraction procedures involving chelating agents such as EDTA (ethylene-diaminetetraaceticacid), DTPA (diethylene-triaminepentaaceticacid) and the Mehlich reagents were first developed to identify trace-element nutrient deficiencies in near-neutral and calcareous soils used for cropping (Lindsay & Norvell, 1969; 1978; Mehlich, 1984), they are being increasingly used to assess toxicities in metal contaminated soils and mining wastes (Gough *et al.*, 1980; Haq *et al.*, 1980; Severson & Gough, 1983; Norvell, 1984; Ma & Lindsay, 1993; Hetrick *et al.*, 1994; Shetty *et al.*, 1994). Since plants exhibit considerable genetic variation in their ability to tolerate non-essential metals such as Cd and Pb the need to quantify the bioavailability of such elements is now recognised as being extremely important (Salisbury & Ross, 1992).

Although a number of chelating agents can effectively complex Cu and Zn in soils, DTPA is one of the most commonly used owing to its ability to effectively chelate Fe and Mn (Lindsay & Norvell, 1978; Neuman *et al.*, 1987). The extraction method of Lindsay & Norvell (1969) has been successful with acid and reduced soils far beyond the original scope of the application, due mainly to the versatility of DTPA, which

provides effective chelation of a wide spectrum of metal cations, including the highly insoluble ferric ion (Norvell, 1984).

Chelating agents function as metal extractants by complexing free metal ions in solution. This reduces the activity of free metal ions in solution and in response metal ions desorb from soil surfaces or dissolve from labile phases to replenish the solution. The amount of chelated metals that are extracted from soils depends largely on two factors, (1) the activity of the metal ions in the soil and (2) the ability of the soil to replenish those ions (Lindsay & Norvell, 1978). Research has shown that environmental factors such as length of shaking, pH, temperature and DTPA concentration significantly influence the amount of metal cations extracted by DTPA (Lindsay & Norvell, 1978; Joshi *et al.*, 1983; Norvell, 1984). Lindsay & Norvell (1978) found that by increasing the concentration of the DTPA extractant a greater amount of metal could be extracted from soils, due to more stress being placed on the labile metal phases. Increasing pH was also found to dramatically decrease the concentrations of Mn and Fe extracted.

The use of DTPA to assess the plant availability of metals in acidic and metal contaminated soils has, however, been called into question in several studies (Dudas & Pawluk, 1977; Gough *et al.*, 1980; Haq *et al.*, 1980; Norvell, 1984). Research indicates that for strongly acid and metal enriched soils, the DTPA extraction procedure of Lindsay & Norvell (1969) may be unsuitable because it involves buffering the soil at pH 7.3 and the addition of CaCl_2 to preclude the dissolution of CaCO_3 and the release of occluded nutrients (Lindsay & Norvell, 1978; Gough *et al.*, 1980; Norvell, 1984). Norvell (1984) suggests that by doing so, the extraction of metals from acid soils may be retarded or otherwise altered to the extent that estimates of plant-availability are distorted. It is also suggested that the pH-buffering capacity of the buffer used in the procedure (0.1M triethanolamine) is not adequate to maintain a relatively constant pH when strongly acid soils are extracted due to the fact that these soils often contain sufficient titratable acidity to neutralise most or all of the remaining conjugate base of the buffer (Norvell, 1984).

Additionally, Norvell (1984) found that the concentrations of DTPA and extractant to soil ratio of 2:1 recommended by Lindsay & Norvell (1969) is not always sufficient to extract all of the plant available micronutrients in metal rich soils. Adjustments in the concentration of the agent, the number of extractions and the soil to extractant ratio may be required so as to facilitate comparison with other soils. Lindsay & Norvell (1978) state that in the vicinity of 600 ppm of Cu, Fe, Mn and/or Zn would be required to saturate the amount of DTPA used in soil tests. Although the chelating capacity is generally sufficient when dealing with uncontaminated soils, it is suggested that the Tui tailings could potentially saturate the DTPA exchange sites.

Research undertaken by Joshi *et al.*, (1983) investigating the influence of several soil parameters on DTPA extractable micronutrients found that CaCO_3 content, the reduction-oxidation status and soil pH exert major influences on the availability of Fe and Mn in soils. Lindsay & Norvell (1978) suggested that if DTPA is to be used to extract Zn in soils with pH below 7.0, inclusion of pH in the regression equation should be considered due to the solubility of Zn being strongly pH dependent. While investigating the utility of EDTA and DTPA in range of diverse soils, Gough *et al.* (1980) also found a strong relationship between soil pH and metal concentrations in plants.

Based on this assessment of previous research it was decided not to proceed with the use of a chelating agent such as DTPA to assess the bioavailability of metals in the Tui Mine tailings. Although DTPA has great potential as an extractant for Zn and Cd on mined land, its suitability for such purposes has not been adequately assessed and the influence of variables such as pH, CEC and organic matter content is not fully understood (Haq *et al.*, 1980; Safaya *et al.*, 1987). Research by Norvell (1984) found that the use of chelating agents was limited when extracting metal-rich soils at low pH. Considering the fact that the Tui tailings are both acidic and metal-rich, the assessment of the bioavailability of the metals in the tailings using DTPA would have involved considerable experimentation beyond the scope of this study.

(ii) Dilute Acids

Varying concentrations of a wide range of acid extractants, including acetic (CH_3COOH), nitric (HNO_3), sulphuric (H_2SO_4) and hydrochloric (HCl), have been used to estimate the availability of plant micronutrients such as Cu, Fe and Zn in soils (Dudas & Pawluk, 1977; Lagerwerff, 1971; Haq *et al.*, 1980; Baker & Amacher, 1982; Haynes & Swift, 1985a, 1985b). Amongst these extractants, dilute HCl and CH_3COOH are two of the most commonly used.

The results obtained through the use of CH_3COOH -based extractants in the determination of 'soil' metal concentrations are like that for majority of acid extractants, highly variable and in many cases contradictory. Although some research suggests the use of dilute CH_3COOH (commonly $0.5M$) as an extractant results in an overestimation of plant available concentrations of soil elements, other research outlined by Brooks (1987) demonstrated that bioassay data for several elements agreed well with values obtained from CH_3COOH extraction. Haq *et al.*, (1980) also found dilute CH_3COOH to be a useful extractant. Their study looked at nine different extractants in an attempt to find a suitable one for estimating the plant-available Zn, Cd, Ni and Cu content metals in metal-contaminated soils. Although none of the extractants investigated proved suitable for all four metals, 0.5 N acetic acid was found to be the best extractant for estimating plant available Cd and Ni, with only pH being required as an independent variable (Haq *et al.*, 1980).

Acetic acid has also been used as a sulphate extractant in a study that assessed the potential acidity of colliery spoils (Pulford & Duncan, 1978). The authors stated that although $0.5M$ acetic is unlikely to extract sulphate present as jarosite or other basic iron and aluminium sulphates, it does extract the more soluble forms. The inability of acetic acid to solubilise some forms of sulphate is attributable to it being a relatively weak acid that does not fully dissociate in aqueous solution, as indicated by its small acid dissociation constant ($K_a = 1.8 \times 10^{-5}$). Using K_a it is possible to calculate the hydrogen ion concentration and hence pH of a $0.5M$ solution of acetic acid as follows;

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][CH_3OO^-]}{[CH_3COOH]}$$

If we let x equals the number of moles of acetic acid that dissociates and assume it is very small compared to the initial concentration of acetic acid ($0.5M$) then the above equation can be simplified to;

$$\frac{x^2}{0.50} = 1.8 \times 10^{-5}$$

$$\therefore x = [H^+] = 3.0 \times 10^{-3}$$

$$pH = -\log [H^+]$$

$$\therefore pH = 2.52$$

Unlike acetic acid, hydrochloric acid (HCl) is a strong acid that becomes fully ionised in solution (eg. $HCl \rightarrow H^+ + Cl^-$). The full dissociation of this solvent results in the acidity of dilute HCl being far greater than that of dilute acetic acid solutions at comparable concentrations. The pH of a solution of $0.1M$ HCl for example has a pH of 1.0.

Dilute HCl has been extensively used as an extracting agent to investigate the plant-availability of heavy metals in soils and uptake by plants (Nelson *et al.*, 1959; Lagerwerff & Specht, 1970; Kinehiro & Sherman, 1967; Lagerwerff, 1971; Takijima & Kasumi, 1973; John, 1974; Dundas & Pawluk, 1977; Norvell, 1984; Haynes & Swift, 1985a; 1985b). Neuman *et al.*, (1987) state that for Cu, more extraction and calibration work has been conducted with HCl than with any other acid.

Lagerwerff (1971) who used a solution of $1M$ HCl to investigate the uptake of cadmium, lead and zinc from soils was prompted to use this extractant for two reasons:- (1) as a fully dissociated acid lacking oxidising qualities it provided H^+ for exchange and limited dissolution in a non-destructive manner, (2) $1M$ HCl is a strong complexing agent for certain transition-group metals such as Cd and Pb. Lagerwerff (1971) suggested that the extractable ion concentrations determined by $1M$ HCl provided useful reference levels to which the amounts of ions absorbed by plants could be related. The acid extractant, however, was found to demonstrate little relationship between non-polluted soils and plant uptake. The failure of this extractant to adequately predict metal uptake is presumed to reflect that at a $1M$ concentration HCl is likely to have solubilised

some non-labile forms of metal such as that occluded in oxides and secondary clay minerals (Ure, 1995).

In most investigations where HCl is used to assess the bioavailability of metals, it is generally used in weaker concentrations. Extractant solution concentrations of 0.1M HCl have long been commonly used to assess the bioavailability of various metal cations in soil media (Viets & Boawn, 1965; Kanehiro & Sherman, 1967; Wear & Evans, 1968; Norvell, 1984; Haynes & Swift, 1985a, 1985b). Norvell (1984) compared the ability of 0.1M HCl to extract Al, Fe, Mn, Zn, Cu, Cd and Ni from diverse soil materials with 5 chelating agents. He observed that 0.1M HCl was the most severe extractant, particularly for Al, Fe and Mn which are often present in part as acid soluble oxides. For this reason it is generally accepted that dilute HCl is a relatively harsh solvent that liberates most forms of labile metals that are available for plant uptake.

Based on previous research (Norvell, 1984; Haynes and Swift, 1985a & 1985b) and the fact that the Tui mine tailings contain negligible organic matter, it was predicted that 0.1M HCl would not only provide useful information relating to the availability of metal to plants but would also satisfactorily estimate non-sulphidic metal concentrations in the tailings. It was postulated that unlike dilute acetic acid solutions (Pulford & Duncan, 1978), 0.1M HCl would be sufficiently harsh to render most forms of Cu and Fe sulphate in the tailings soluble without significantly affecting the stability^{cf} sulphide minerals in the tailings.

3.4.2.3 Total Metal Extractants

Techniques used to measure the total heavy metal contents of soils may be broadly divided into two categories:- (1) single-element methods such as flame atomic absorption spectrometry (FAAS) or (2) multi-element methods such as inductively coupled plasma-atomic emission spectrometry (ICP-AES) or X-ray fluorescence spectrometry (XRFS) (Ure, 1995). Some multi-element analyses were conducted on the Tui tailings using ICP-AES, however, most elemental analyses were conducted using FAAS as these methods were simple and accurate. Although dilution arising from sample preparation limits the ability of atomic absorption spectrometry to detect some

trace elements in non-contaminated soils, the tailings were well suited to this technique due to their metal-rich nature.

A variety of extractants are used to estimate the total levels of heavy metals in contaminated soils and mining wastes. These include *aqua regia*⁸ (Van Loon & Lichwa, 1973; Haq *et al.*, 1980; Smith, 1994), concentrated nitric acid (Smith & Bradshaw, 1979; Clevenger, 1990; Whitely & Williams, 1993), multi-acid extractants (Ure, 1995) and hydrofluoric acid based extractants (Ward *et al.*, 1977; Safaya *et al.*, 1987, Neuman *et al.*, 1987).

Because most soils contain substantial amounts of silicates, total dissolution generally requires the use of an HF-based extractant which is capable of attacking silicate minerals (Ure, 1995). Concentrated acids such as nitric (HNO₃) and/or perchloric acid (HClO₄) are often used in combination with HF as a pre-treatment to oxidise organic matter and sulphide minerals (Lim & Jackson, 1982; Safaya *et al.*, 1987; Ure, 1995; Kucha *et al.*, 1996).

Where the vast proportion of metals are not bound up in the silicate lattice of the material, drastic attack with HF acid may not be necessary and pseudo-total analyses can be carried out using strong acids such as HCl, HNO₃, HClO₄ either singularly or in combination (Ure, 1995). Although these acids do not dissolve silica or silicates completely, they are sufficiently vigorous to dissolve non silicate-bound heavy metals, in the form of sulphide minerals for example (Smith & Bradshaw, 1979). Sulphuric acid, in contrast, is poorly suited to FAAS analysis because of its complex interference effects. Losses of Pb as insoluble PbSO₄ may also occur and other elements may be lost by occlusion in precipitated CaSO₄ in calcium-rich soils (Ure, 1995).

⁸ A mixture of concentrated nitric and hydrochloric acids (1:3 v/v).

Aqua regia is probably the most widely used extractant adopted for pseudo-total soil analysis (Ure, 1995). The extractant generally removes between 70 and 90% of heavy metals in soils. Research outlined by Ure (1995), however, indicates that strong acids such as concentrated HCl, HNO₃ are generally equally effective as *aqua regia* at extracting similar levels of Cd, Cu, Mn, Ni, Pb and Zn from metal contaminated soils. Smith & Bradshaw (1979) found that the use of 25% (v/v) HNO₃ in a quick extraction procedure extracted about 90% of the metal from sulphidic mining wastes.

3.5 Acid Mine Drainage Treatment

Clearly the most effective way of preventing Acid Mine Drainage (AMD) is to ensure acid generating materials are completely isolated from oxidising conditions and iron-oxidising bacteria. Unfortunately, this approach is not always possible and has certainly not always been used in past mining operations. Thus drainage water derived from mining sites often requires treatment prior to discharge to reduce its impact on the aquatic environment. The long term cost of treating AMD can be extremely expensive (Skousen *et al.*, 1990; Hellier *et al.*, 1994; Skousen & Larew, 1994) and is a cost too often burdened on the ratepayers of historic mining communities.

Fortunately a variety of effective technologies has been developed to treat AMD. These include neutralisation, reverse osmosis, low pressure ultra-filtration, bacterial facilitated sulphate reduction, evaporation, co-disposal with domestic wastes, anoxic limestone drains (ALDs), anaerobic (organic substrate) wetlands and aerobic wetlands (Bell *et al.*, 1982; Hedin *et al.*, 1994). Research into the use of ion exchange resins and natural and synthetic zeolites in the treatment of AMD also shows promising results and signal that these materials are likely to be increasingly used in the removal of metals from contaminated mine drainages (Schultze *et al.*, 1994; Riveros, 1995).

3.5.1 Active Treatment

Neutralisation is the most widely used method of active AMD treatment. In principle it is a simple technique that involves the addition of a base to the AMD to reduce acidity, increase alkalinity and precipitate Fe, Al and various heavy metals (Bell *et al.*, 1982). In practice, however, the great variability in the composition of AMD and the different effluent quality requirements often precludes the application of simple neutralisation

techniques (Bell *et al.*, 1982; Skousen *et al.*, 1990). In the past, attempts to improve water quality were often rudimentary and involved diverting AMD firstly into settling ponds and then through porous limestone barriers. In the United Kingdom this method was found to be “*notoriously unsuccessful*” as the limestone beds were often rapidly clogged with reaction products such as $\text{Al}(\text{OH})_3$, FeOOH , $\text{Fe}(\text{OH})_3$, rendering them ineffective (Palmer, 1991).

Most modern neutralisation techniques typically involve a several step process in which a variety of reagents including, alkali reagents flocculants and oxidants may be added to both aerated and standing ‘water’ (Skousen *et al.*, 1990; Murdock *et al.*, 1995). Many different base additives have been used in the treatment of AMD but the most commonly used alkalies are hydrated lime ($\text{Ca}(\text{OH})_2$), limestone (CaCO_3), sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) (Bell *et al.*, 1982; Skousen *et al.*, 1990). Each chemical has its advantages and disadvantages and the selection of a suitable chemical or combination of chemicals depends on the geochemistry of the AMD being treated. Where Fe^{2+} is present in high concentrations for example, oxidising agents such as hydrogen peroxide, potassium permanganate and calcium hypochlorite may be used to speed the oxidation of Fe^{2+} to the less soluble Fe^{3+} form (Skousen *et al.*, 1990).

Whilst neutralisation methods are effective at ameliorating water quality, they can substantially increase the hardness of effluents and result in the production of large quantities of potentially toxic sludge which is characteristically difficult to ‘handle’ and dewater. Chemical costs are ongoing and can be particularly high if the AMD contains high concentrations of Fe^{2+} and Mn^{2+} (Evangelou, 1984; Skousen *et al.*, 1990).

3.5.2 Passive Treatment

The treatment of contaminated mine drainage using passive treatment systems is currently the focus of considerable research and shows great promise for long-term, low-cost treatment of contaminated water from degraded mine sites (Brodie & Hedin, 1994; Hedin & Watzlaf, 1994; Hedin *et al.*, 1994; Kepler & McCleary, 1994; Skousen & Ziemkiewicz, 1995). Passive treatment technology has been chiefly developed by staff at the US Bureau of Mines and to date has been used primarily in the treatment of AMD

originating from colliery spoil in the US coal fields. The technology does, however, show promise for use in the treatment of AMD from metalliferous mines (Eger *et al.*, 1994)

There are currently three principal types of passive treatment systems; *aerobic* and *anaerobic wetlands* and *anoxic limestone drains*. These systems exploit natural chemical and biological processes that ameliorate water contamination. The primary advantages of these systems are that in theory they generally require fewer chemical reagents and less operational attention and thus provide a more cost-effective, long term means of treating metal contaminated mine drainage (Hedin *et al.*, 1994; Hellier *et al.*, 1994).

3.5.2.1 Anoxic Limestone Drains

The technology of anoxic limestone drains (ALDs) is still very much in its infancy. Turner & McCoy (1990) were the first to describe the use of buried limestone beds to treat AMD. They function by promoting the contact of AMD with limestone under anoxic conditions and are designed to increase the water's bicarbonate alkalinity and pH to circumneutral levels (6 to 7). ALDs currently being used to treat AMD in the mining industry are typically about 60 m long and 1 m² in cross-section. They often contain about 70-80 tonnes of high grade limestone in the form of 5 to 10 cm diameter cobbles (Brodie & Hedin, 1994). The limestone cobbles are usually contained in geofabric or high density plastic lining that is buried within compacted clay soils or substrates to prevent the ingress of oxygen.

ALDs are typically designed to retain water for about 15 hours, a time usually sufficient to allow the water to attain an alkalinity level of approximately 300 mg/L. Current design guidance precludes the use of successive ALDs to generate alkalinity much in excess of this value because of concerns with dissolved oxygen (Kepler & McCleary, 1994).

After exiting the ALD the water is usually fed into an aerobic pond which promotes the precipitation of metals via hydrolysis as ferrous iron is oxidised. The water's induced bicarbonate alkalinity is designed to neutralise the acid produced by the hydrolysis of Fe^{3+} (Hedin & Watzlaf, 1994; Hedin *et al.*, 1994).

One of the main limitations of ALDs is that they are poorly suited to mine drainage that contains appreciable concentrations of dissolved Fe^{3+} , Al, or oxygen (>2 mg/L). The presence of these constituents in water entering an ALD is likely to result in the formation of FeOOH , $\text{Fe}(\text{OH})_3$ and/or $\text{Al}(\text{OH})_3$ which tend to rapidly block the drains (Hedin *et al.*, 1994; Robb & Robinson, 1995). Failure to identify high concentrations of dissolved Al levels in input waters has seen ALDs constructed in Pennsylvania fail within the first 4 months of use due to the formation of $\text{Al}(\text{OH})_3$ (Brodie & Hedin, 1994). Similar problems may arise with the formation of CaSO_4 if sulphate levels in the AMD exceed about 4000 mg/L. The maintenance of anoxic conditions in the drains is crucial in that it inhibits the oxidation of Fe^{2+} and therefore limits the likelihood of ferric hydroxide formation (Hedin *et al.*, 1994).

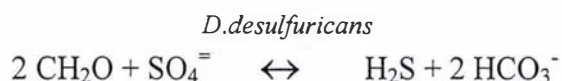
Since the function of ALDs is based on the dissolution and thus removal of limestone they have a finite working life. Whilst many ALDs are currently constructed with sufficient limestone to theoretically function for 20 to 30 years, plugging by metal hydroxides is likely to result in hydrologic failure of the ALD well before the limestone is exhausted (Hedin *et al.*, 1994).

3.5.2.2 Aerobic & Anaerobic Wetlands

As alluded to above, ALDs are often used in conjunction with aerobic wetlands which are also useful for facilitating the precipitation of metals (particularly Fe and Al) from circumneutral mine drainage. Aerobic wetlands are designed to encourage the oxidation of Fe^{2+} to Fe^{3+} which is highly insoluble at pH levels above about 3 (Hedin *et al.*, 1994). They are consequently typically shallow (<1 m) in construction and are designed to aerate the water and dissolved constituents.

In contrast to aerobic treatment ponds, anaerobic wetlands are constructed to promote the activity of anaerobic bacteria which precipitate metal sulphides and generate bicarbonate alkalinity (Eger *et al.*, 1994; Hedin *et al.*, 1994; Hellier *et al.*, 1994). The wetlands are typically lined with up to 0.5 m of organic-rich material such as spent mushroom compost, manure, composted sewage sludge and sawdust. Organic substrates are often stabilised with vegetation such as cattails (*Typha latifolia*) which also contribute organic matter and enhance anaerobic conditions (Hedin *et al.*, 1994).

The organic material in anaerobic wetlands is designed to accommodate sulphate reducing bacteria such as *Desulfovibrio desulfuricans* which can reduce sulphate in mine water to produce hydrogen sulphide (H₂S) and bicarbonate gas (HCO₃⁻) as per the following equation:



The resulting H₂S reacts with heavy metals in mine drainage causing them to precipitate as sulphides as exemplified by the following equation:



Although acidity is produced during the precipitation of sulphides the alkalinity produced by the reduction of sulphate to H₂S buffers against pH change to help maintain circumneutral to alkaline conditions (Robb & Robinson, 1995). The pH buffering of this system is important because sulphate reducing bacteria will not flourish below pH 5.0. Limestone is usually added to organic substrates to introduce an additional source of bicarbonate and to further ensure that circumneutral pH levels are maintained in the wetland (Hedin *et al.*, 1994)

Where the pH of the water entering the wetland system is >4, anaerobic wetlands are often preceded by a single aerobic pond to precipitate Fe. This encourages the subsequent precipitation of Mn and other heavy metals in the anaerobic wetland. Manganese can be difficult and/or costly to remove in both passive and active treatment systems because unlike Fe²⁺ no natural mechanism exists to rapidly oxidise Mn²⁺ under acidic conditions. In anaerobic wetlands Mn is usually precipitated as MnO₂ but this is

unlikely to occur unless other metals are present in minor amounts and pH levels are maintained above 6.0 (Robb & Robinson, 1995).

Anaerobic wetlands provide a viable means of treating drainage waters containing dissolved oxygen, Fe, Al and/or high acidity concentrations (>300 mg/L) which can not be treated using ALDs (Hedin *et al.*, 1994). Their biggest limitation, however, is that they require a relatively large surface area of land for operation (at least six times the area required by aerobic wetlands constructed to treat alkaline waters) (Hedin *et al.*, 1994). The surface area requirements of anaerobic wetland systems often exceed 1 ha and are governed by the volume and metal loading of the mine drainage.

Much of the current research associated with passive treatment systems is focusing on the development of 'hybrid' ALD-compost wetlands or SAPs (Successive Alkalinity Producing Systems) (Kepler & McCleary, 1994). The theory behind these systems is that organic substrates can be used to strip Fe^{3+} and dissolved oxygen from the contaminated water to facilitate the flow of water into underlying anoxic limestone drains (Hedin *et al.*, 1994; Kepler & McCleary, 1994). If these systems are successfully developed it may be possible in the future to cost-efficiently treat highly acid mine drainages by cycling them between anoxic alkalinity-generating environments and aerobic metal-removing environments (Hedin *et al.*, 1994). SAPs also have the added benefit of requiring substantially less surface area than anaerobic wetlands and are capable of generating much higher levels of alkalinity (Kepler & McCleary, 1994).

Useful reviews of the use of wetland areas and passive treatments systems in the treatment of AMD are provided by Sengupta (1993) and Hedin *et al.* (1994).

3.6 Preventing Acid Mine Drainage

From the preceding literature review it is evident that *iron-oxidising bacteria*, *oxygen* and *water* all play a vital role in the oxidation of sulphide minerals and ultimately in the production of AMD. Whilst there is a wide variety of techniques employed to prevent mine wastes from generating AMD, the methods are similar in that most try to eliminate either bacteria, oxygen and/or water from the oxidation system.

Methods used to control or limit the ingress of oxygen into sulphide-bearing materials include; deep burial, subaqueous deposition, organic matter application, vegetative covers, compacted clay and synthetic barriers. Barrier methods, pH modifiers (including alkaline recharge zone techniques) and bactericides are commonly used to inhibit the activity of iron-oxidising bacteria. The ingress of water into sulphidic wastes is often minimised via the use of diversion drainage systems, impermeable clay and synthetic barriers and/or vegetative covers.

The re-mining of sulphide deposits and/or the selective removal and treatment of acid generating sulphide minerals are also methods that are being researched and used at some sites (Raicevic, 1979; Caruccio *et al.*, 1990; Humber & Eng, 1995). The sulphide content of tailings may be reduced by means of bulk sulphide flotation prior to placement (Sengupta, 1993). Considerable research is also being focused on the use of hyperaccumulating plants for phytoremediation of metal contaminated soils and mine wastes (Brooks, 1987; Baker *et al.*, 1988, 1995; Chaney *et al.*, 1995; Nicks & Chambers, 1995; Reeves *et al.*, 1995). The primary factor currently limiting the application of phytoremediation is the need to find rapid growing, high biomass crops that can hyperaccumulate problematic metals such as Cu, Pb and Zn. Research currently being undertaken at Massey University is investigating the combined use of chelating agents and non-hyperaccumulating plant species to phytoremediate metal contaminated soils (Brooks, *pers. comm.*).

Two novel approaches to prevent sulphide oxidation are micro-encapsulation⁹ of sulphides with FePO₄ (Backes *et al.*, 1987; Pulford, 1991; Huang & Evangelou, 1992; Evangelou, 1994; Georgopoulou *et al.*, 1995) and cathodic protection of sulphide-bearing deposits (Shelp *et al.*, 1995). Although both technologies are in the developmental stage, laboratory and small scale fields studies indicate that they show potential for inhibiting sulphide oxidation and arresting the formation of AMD.

⁹ Micro-encapsulation techniques exploit the ability of some compounds such as FePO₄ to form protective films on the surface of sulphide grains. Their formation effectively inhibits sulphide oxidation by preventing the attachment of iron-oxidising bacteria and by reducing oxygen contact.

3.6.1 Subaqueous & Subterranean Deposition

Clearly one of the most successful and cost effective means of preventing the oxidation of sulphide-bearing wastes is to selectively bury such materials and preferably encapsulate them in low permeability material. This method is commonly used to isolate reactive (acid generating) material and often simply involves identification and selective handling of reactive material during mining operations (Geidel & Caruccio, 1984). The handling difficulties involved with tailings may preclude their disposal by deep burial although redeposition into underground workings and/or open pits has been practiced at some sites (Harries & Ritchie, 1988).

The blending of acid-generating and acid-consuming rock units is also used at some sites as an alternative to adding neutralising agents to the acid-generating waste during operations and waste placement (Sengupta, 1993; Skousen & Larew, 1994).

Subaqueous tailings deposition is a method used to minimise oxygen diffusion into the acid generating tailings. It is being increasingly used in North America and involves the disposal of tailings into existing bodies of water (Pedersen *et al.*, 1994) or alternatively flooding subaerial tailings deposits upon abandonment (Davé & Vivyurka, 1994; St-Arnaud, 1994). Marine disposal of pyritic wastes has been used at mining sites in Norway (Sengupta, 1993) and is likely to be used at Lihir gold mine in Papua New Guinea (PNG) once ore processing operations commence (Harris, 1997). Although river systems are not commonly used as depositories for pyritic materials in most current mining operations, river disposal is used in some Third World countries as a cheap alternative to terrestrial dumping. Mining operations at the Bougainville copper mine in PNG, for example, involved the disposal of an estimated 510 million tons of tailings into the Kawerong/Jaba river-system between 1972 and 1985. The extent of dumping was on such a large scale that a 7 km² marine delta formed 30 km from the mine site at the mouth of the river-system (Archer *et al.*, 1988). Whilst river disposal of tailings continues to be used at the Porgera (gold) and Ok Tedi (copper) mines in PNG, little is known about its efficacy at controlling sulphide oxidation (Harris, 1997).

Water, with its low oxygen diffusion coefficient (2×10^{-9} m²/s) and inability to dissolve large quantities of oxygen (8.6 g/m³ @ 25 °C) is, however, considered to be one of the

most effective oxygen-limiting covers for sulphidic wastes (Davé & Vivyurka, 1994). Even partial saturation of tailings is likely to substantially reduce sulphide oxidation as the rate of oxygen diffusion through water is approximately 10,000 times less than through air (James & Eng, c.1992). The rate of oxygen transport through water is thus considered to be sufficiently low to be of “*no concern in terms of acid generation*” (Sengupta, 1993).

This type of disposal is considered to be suitable at locations where the topography “*lends itself to stable containment against hydrostatic pressure*” (Ritcey, 1989) and obviously where evapotranspiration is less than rainfall and/or inflow of water into the impoundment. The advantages associated with subaqueous disposal include:- (i) limits oxygen and hence controls acid generation, (ii) the water body acts a sedimentation basin, (iii) outlet drainage flows can be controlled, (iv) eliminates surface erosion by wind and water action, (v) temperature reduction can occur and inhibit bacterial activity and (vi) facilitates bacterial reduction of nitrates and sulphates (Garga *et al.*, 1983; Davé & Vivyurka, 1994).

The disadvantages of water covers include the need to ensure the water is adequately contained and protected against flood and the potential for infiltrating water to destabilise materials (via increased interstitial pore pressures) and/or to act as a conduit for contaminants (Garga *et al.*, 1983).

3.6.2 Bactericides

Singer & Stumm's (1970) suggestion that acid mine drainage may best be controlled by inhibiting the bio-catalytic oxidation of Fe^{2+} to Fe^{3+} is perhaps the reason for much of the research into the development of bactericides. Studies investigating the use of bactericides in land reclamation indicate that they are useful agents for reducing sulphide oxidation and acid mine drainage (Kleinmann *et al.*, 1980; Watzlaf, 1986, 1987, 1988; Parisi *et al.*, 1994; Splittorf & Rastogi, 1995). Many types of bactericides are used in the mining industry to inhibit sulphide oxidation including, food preservatives (benzoate and sorbate compounds), phosphate compounds and anionic surfactants such as sodium lauryl sulphate and dodecylbenzene sulphonate (Sengupta, 1993; Parisi *et al.*, 1994).

The primary purpose of most bactericides is to create conditions that inhibit the activity of the bacterium *Thiobacillus ferrooxidans* which is responsible for the catalytic oxidation of Fe^{2+} to Fe^{3+} . As discussed in section 3.3, the formation of Fe^{3+} is considered to be the rate limiting step involved in the oxidation of pyrite. Many bactericides inhibit the biocatalysis of pyrite by inducing physico-chemical conditions that prevent micro-organisms from attaching to the mineral surfaces and/or by detrimentally altering the permeability of the cells' cytoplasmic membrane (Kleinmann *et al.*, 1980; Ritcey, 1989; Pulford, 1991).

Since bactericides do not usually effect the abiotic oxidation of sulphide minerals, they do not eliminate AMD and are thus generally used in conjunction with other AMD control techniques (Sengupta, 1993; Splittorf & Rastogi, 1995).

One common drawback with most bactericides is that they degrade rapidly with time and are potentially depleted by runoff and leaching. To overcome this problem bactericidal compounds are often impregnated into rubber pellets or encapsulated in plastic pellets formulated to slowly degrade with time (Kleinmann *et al.*, 1980; Sengupta, 1993; Splittorf & Rastogi, 1995). The time-release bactericide *ProMac* (developed by BF Goodrich) is one most widely used commercial bactericides in the mining industry (Sengupta, 1993). Overseas research outlined by Sengupta (1993) indicates that ProMac can improve water quality by significantly reducing metal concentrations, acidity and sulphate levels and encourage the establishment of plants and heterotrophic bacteria populations.

The high cost of applying bactericides (often in the order of several thousand dollars per hectare) and the recognised need to use these substances in conjunction with other forms of sulphide oxidation control techniques are considered to be two of the primary drawbacks associated with the use of bactericides (Sengupta, 1993). Additionally, research outlined by Watzlaf (1988) indicates that bactericides may be ineffective when applied to partially oxidised materials. This finding indicates that bactericides may be ineffective at significantly inhibiting the formation of AMD at the Tui mine site.

3.6.3 pH Modification

The surface application and/or incorporation of acid neutralising compounds is the most commonly used method for treating pyritic mining wastes¹⁰. In principal base addition is designed to inhibit sulphide oxidation by precipitating Fe^{3+} and by creating an environment that is not conducive to the growth of iron-oxidising bacteria which oxidise Fe^{2+} to Fe^{3+} . As discussed in section 3.3, the rate of sulphide oxidation (and hence AMD formation) is believed to be dramatically reduced in the absence of soluble Fe^{3+} . Research outlined by Ziemkiewicz & Skousen (1995), however, indicates that the addition of alkaline materials may not significantly inhibit sulphide oxidation. Instead they suggest that sulphide oxidation may continue largely unhindered and that AMD is mitigated by the precipitation of metals (primarily as hydroxides) under alkaline conditions.

The most commonly used base additives are calcite (CaCO_3), burned lime (CaO), hydrated lime $\text{Ca}(\text{OH})_2$ and sodium hydroxide (NaOH) (Sengupta, 1993). These and other bases may be added in 'pure' chemical form or as constituents in a variety of industrial wastes that are increasingly being used to amend acid-generating mine wastes. Trials investigating the use of alkaline waste products such as lime kiln dust (Rich & Hutchison, 1994; Evans & Rose, 1995; Ziemkiewicz & Skousen, 1995), coal combustion byproducts (Dick *et al.*, 1994; Ziemkiewicz & Skousen, 1995) and Leblanc waste¹¹ (Gemmell, 1981) indicate they are useful pH amendments and may be an extremely cost effective means of controlling AMD where a ready source is available. An added benefit of using wastes rich in CaO (eg. lime kiln dust) is that they increase the shear strength of saturated or semi-saturated tailings within a few weeks of application (Ritcey, 1989).

¹⁰ See section 3.7.3 for discussion pertaining to the use of limestone in the reclamation of pyritic mine wastes.

¹¹ The Leblanc process (now obsolete) was used to produce Na_2CO_3 for glass manufacture. The process produced highly alkaline (pH 12.7) waste containing large quantities of calcium hydroxide and calcium carbonate (Gemmell, 1981).

The success of base additives at controlling AMD depends primarily on:- (i) the path of water through the system, (ii) the nature (eg. duration) of contact of acid generating rock and pore waters with the neutralising agent, (iii) the proportion of excess alkalinity and (iv) the type and purity of the neutralising agent (Gemmell, 1981; Costigan *et al.*, 1984; Sengupta, 1993). AMD is usually best controlled when highly reactive alkaline compounds are thoroughly mixed with the acid source to facilitate 'continual' dissolution of the additive in response to acid generation (Sengupta, 1993). If AMD control is the primary objective of pH amendment, excess neutralising agents should be incorporated to compensate for that lost from the system due to consumption by infiltrating water and by that effectively 'lost' due to armouring by oxidation products (Sengupta, 1993).

Two potential disadvantages associated with the blanket application of neutralising agents in terms of their ability to inhibit the oxidation of sulphide minerals are firstly, that the ameliorant (neutralising agent) is not necessarily concentrated in major water recharge zones and, secondly, that the major flow path of water will not necessarily intercept a large portion of the neutralising agent unless the amended surface is highly permeable. The use of alkaline recharge zones are designed to overcome these problems by intercepting infiltrating water and converting it into highly alkaline solutions which can potentially neutralise acidity and displace iron-oxidising bacteria (Caruccio *et al.*, 1984; Caruccio *et al.*, 1988; Nawrot *et al.*, 1994). Trials which have effectively altered the geochemistry of upslope groundwater recharge zones with alkaline materials including hydrated lime ($\text{Ca}(\text{OH})_2$) and lime (CaCO_3) have shown "*extremely encouraging results*" by reducing seepage acidity by 23% and acidity in recharge zone groundwater by up to 90% (Nawrot, 1994).

3.6.4 Dry Cover Barriers

The capping of sulphidic tailings and wastes with geological or synthetic barriers aims at preventing AMD by firstly restricting the entry of oxygen and/or secondly by preventing the migration of AMD by controlling water (conduit) entry. Since the *Thiobacilli* bacteria involved in sulphide oxidation are micro-aerophilic and can survive at reduced oxygen tensions, partial elimination of oxygen is considered to poorly control AMD (Singer & Stumm, 1970). Thus, barriers are believed to be more effective at

controlling AMD by reducing in the infiltration of water and ultimately preventing the migration of sulphide oxidation products to the surrounding environment.

Barriers vary considerably in their structure and range from simple geological caps constructed of compacted 'soil' to synthetic membrane liners and high technology composite covers.

3.6.4.1 Synthetic Barriers

Synthetic barriers/liners are fabricated from a variety of materials including polyvinyl chloride (PVC), high density polyethylene (HDPE), butyl rubber, asphalt emulsions and cementitious materials (Ritcey, 1989; Sengupta, 1993; Jones & Wong, 1994). They have the potential to provide covers with an extremely low conductivity of oxygen and water. The high cost of installation and their susceptibility to mechanical rupture, however, are major limitations governing their use. To prolong their effective life synthetic liners are often used in conjunction with geological covers designed to host plants and protect the underlying synthetic liners from ultraviolet light and/or the direct effects of trafficking.

Synthetic mineral polymers (geopolymers) are compounds which when added to mineralised tailings achieve strength through molecular bonding (Davidovits & Davidovics, 1987). Under alkaline conditions these aluminosilicate compounds are converted to very reactive silico-aluminates which polycondense to form three dimensional stone-like materials (Ritcey, 1989). Whilst this technology is still in its developmental stage, geopolymers may in the future be used to create low permeability, high strength covers for the long term chemical and physical stabilisation of tailings. Ahmed (1994, 1995) reports on similar studies which are developing techniques to enhance the formation of hardpans which naturally occur in some pyrrhotite-rich tailings. These synthetic hardpans are seen as a potential means of inhibiting water and oxygen ingress into sulphide bearing materials.

3.6.4.2 Geological Barriers

Geological barriers are usually constructed from non-sulphidic geological materials such as overburden, soils and clay substrates (Pulford, 1991; Sengupta, 1993). Single layer barriers constructed of compacted clay or silt have been frequently used to cap and

isolate sulphide bearing materials from infiltrating water and oxygen (Pulford, 1991; Sengupta, 1993). Problems associated with the use of such covers include that:- (i) they are generally only effective at limiting oxygen ingress if they are maintained in a saturated or near saturated state, (ii) they do not prevent capillary rise of contaminated water from underlying materials and (iii) they are prone to erosion (Sengupta, 1993). Compacted geological barriers also tend to be poor growing media for plants and where vegetation does establish penetrating roots can rapidly breach the barrier and facilitate the ingress of air and water to the underlying waste material.

To eliminate problems associated with single-layered geological barriers, composite covers have been developed to cap and isolate acid generating wastes (Harries & Ritchie, 1988; Sengupta, 1993; Bell *et al.*, 1994; Aachib *et al.*, 1994). Composite covers are typically constructed of 3 or 4 layers of geological materials of variable thickness which each have a specific function. Collectively these layers may be a metre or more thick and are often designed to simultaneously host vegetation, inhibit water and air infiltration, prevent capillary rise of contaminated water and to prevent desiccation cracking (Sengupta, 1993).

Wind and water erosion of composite covers is usually prevented by establishing vegetation on the surface of the cover. Thus, a surface horizon with chemical and physical properties conducive to plant growth must be incorporated. Alternatively where vegetation is not used, a coarse gravel layer is usually ^{placed} on the surface of the cover to reduce the effects of erosion. Another main design feature of many composite covers is the incorporation of a capillary break layer that is designed to inhibit the capillary rise of AMD and to prevent the accumulation of metal compounds in the growing medium or at the surface of the cover. This is usually achieved via the use of a layer of coarse textured material such as a screened gravel with no fines. Whilst laboratory studies indicate that a 50 mm layer of gravel may be sufficient to prevent the upward movement of solutes, a 300 mm layer is considered to be more practical minimal depth (Johnson *et al.*, 1994).

Capillary action is also used advantageously within composite covers to create moisture retention zones which potentially store water for vegetation, limit desiccation of underlying layers and reduce oxygen diffusion (Sengupta, 1993). Moisture retention

zones can be created by ‘sandwiching’ a fined grained material between two layers of well sorted coarse gravel. In this situation the middle layer will tend to maintain a comparatively high water content (Aachib *et al.*, 1988).

Infiltration of water and oxygen may be further reduced by the emplacement of a compacted fine-grained geological barrier and/or a synthetic liner immediately above the waste material. The lower the permeability of this layer the more effective the cover will be at reducing infiltration.

Figure 3.2 highlights the theoretical difference in water infiltration between bare tailings and tailings capped with a composite cover consisting of an infiltration barrier, a capillary break/lateral drain and vegetated soil. Mathematical modelling indicates that bare tailings will exhibit high runoff (19%)¹², modest evapotranspiration losses (63.5%) and substantial net infiltration/seepage (17.5%). Capping the tailings with a vegetated composite cover will in theory reduce total seepage by about 62% to 6.6% (Bi Tech Publication, 1989, cited in Sengupta, 1993).

Whilst composite covers are effective at reducing seepage it is important to note that unless they are used in combination with synthetic membranes, infiltration into underlying material will continue and thus AMD is unlikely to be totally arrested (Bi Tech Publication, 1989, cited in Sengupta, 1993).

The Rum Jungle mine site¹³ in Australia is considered to be one of the best documented examples of the use of composite cover technology (Sengupta, 1993). Geochemical monitoring of the pyritic waste dumps at the site indicates that the composite covers have been effective at reducing the ingress of oxygen and particularly water into the dumps. The percentage of incident rainfall infiltrating the dumps was found to fall from about 50% to 60% prior to rehabilitation to just 3% after the emplacement of the covers (Harries & Ritchie, 1988). The composite covers also appear to have reduced Cu, Mn and Zn loading of AMD emanating from the dumps by more than 60% (Sengupta, 1993).

¹² Bracketed values represent percentage of annual precipitation.

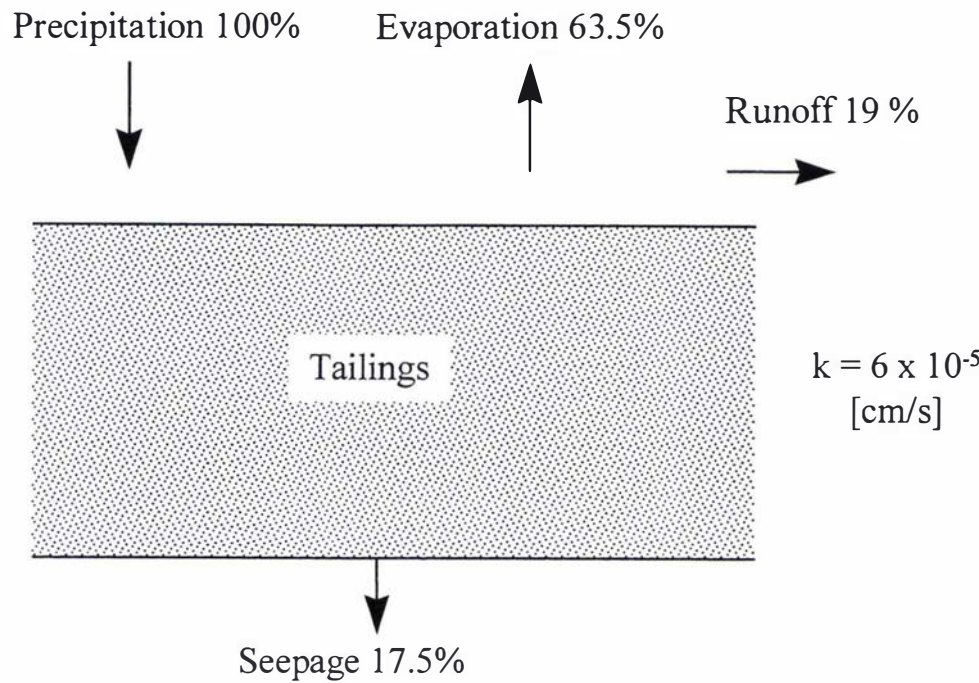
¹³ See section 3.2.1.1 for further discussion of the remedial work carried out at the Rum Jungle mine site.

3.6.4.3 Organic Barriers

The surface application of organic-rich materials onto acid generating mine wastes is another method that has shown promising results in reducing oxygen ingress (Pierce *et al.*, 1994; Tremblay, 1994). Organic barriers are normally constituted of organic wastes such as composted municipal sewage sludge, manure or ligneous wastes including paper pulp and bark. In theory organic barriers reduce sulphide oxidation and AMD by:- (i) acting as a sink for atmospheric and dissolved oxygen which is consumed by heterotrophic microorganisms during organic matter decomposition, (ii) providing a physical barrier to oxygen if high moisture content is maintained in the cover, (iii) producing soluble organic compounds that leach into underlying material and inhibit the growth and metabolism of iron-oxidising bacteria and (iv) by encouraging the activity of sulphate reducing bacteria which precipitate sulphide minerals and lead to the removal of Fe^{3+} from solution (Pierce *et al.*, 1994).

In terms of cost one of the primary advantages of using organic wastes to reclaim mine sites is that the amendment is usually free and haulage and application costs may be offset by savings made with waste disposal.

(a) Bare Tailings



(b) Capped Tailings

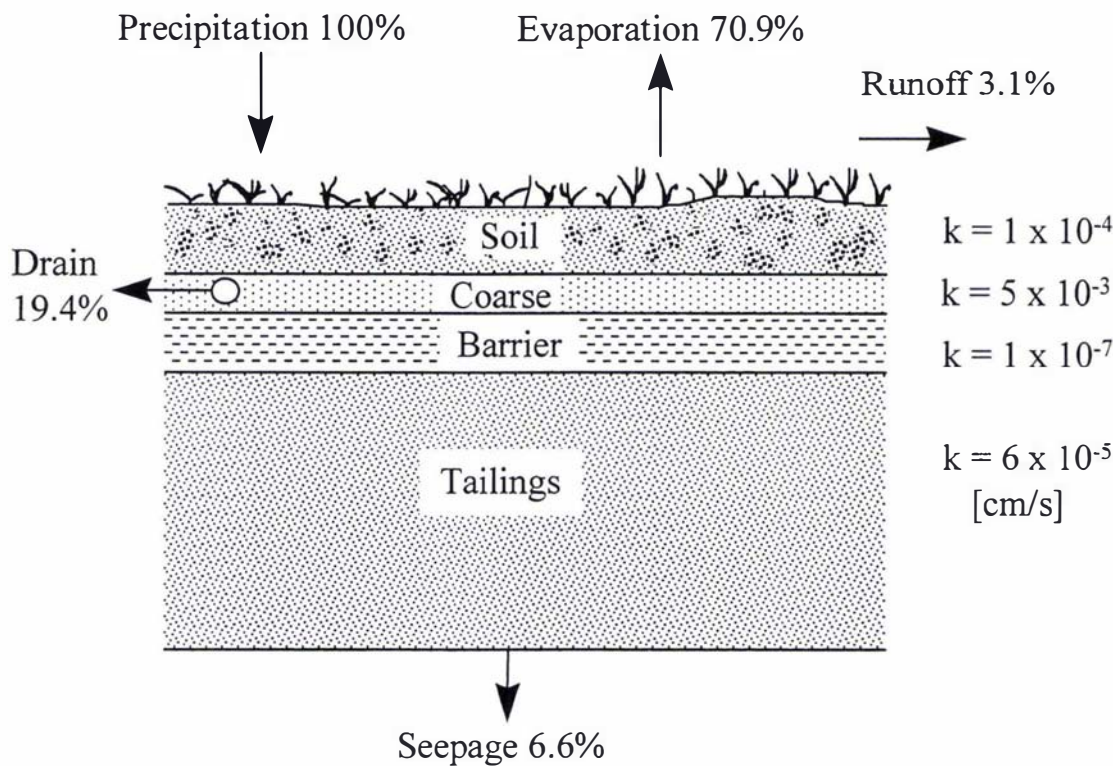


Figure 3.2 Infiltration rate, runoff and seepage for (a) bare tailings and (b) capped tailings.
Material depths:- Soil layer =1.0 m, Coarse layer = 0.3 m, Barrier layer = 1.0 m.
(adapted from Bi Tech Publication, 1989 cited in Sengupta, 1993).

3.7 Revegetative Reclamation

Since the goal of most land reclamation projects is to establish a permanently stable landscape that is aesthetically and environmentally compatible with surrounding undisturbed land, vegetation is often used to reclaim tailings and waste rock dumps (Sengupta, 1993). Ideally vegetative reclamation should produce a self-perpetuating plant cover either directly, or by promoting the colonisation of plants which will form a self-regenerating community (Darmer, 1973). It is widely recognised, however, that wastes from metalliferous mines, particularly acidic tailings, are very difficult to revegetate (Pulford, 1991; Johnson *et al.*, 1994). There are several factors that may inhibit plants from naturally colonising tailings. These include:-

1. Low pH and associated problems with H^+ and metal toxicities.
2. Major plant nutrients, in particular nitrogen and phosphorus, are generally deficient in tailings. *In situ* cycling of nutrients is usually negligible due to the characteristically low organic matter content of tailings.
3. The small uniform grainsize of tailings and lack of macroporosity results in poor soil aeration and drainage.
4. Wind blown tailings particles tend to sand blast, uproot and bury young plants.
5. The thixotropic properties of tailings can make 'handling' and the use of heavy vehicles for amendment application difficult.
6. The high albedo of tailings may impose physiological stress on growing plants (Easton-Groves *et al.*, 1982; Palmer, 1991)

To gain the full aesthetic and practical benefits of a vegetative cover, the cover should be continuous, dense and permanent. Research outlined by Sengupta (1993), investigating the natural recolonisation of three abandoned lead and zinc tailings deposits in Wisconsin, USA, found that aggregation of vegetation was extremely pronounced at the sites and that numerous bare areas existed interspersed with well-vegetated zones. This type of patchy vegetative cover is commonly observed on colliery spoil and metal contaminated sites where acidification and/or metal toxicity restricts the colonisation of plants or causes plant 'die-back' (Costigan *et al.*, 1981; Winterhalder, 1995b).

Some of the earliest research into the establishment of vegetative covers over fine-grained mine wastes began in the South African Witwatersrand in the early 1930s, where attempts were made to suppress dust from nearly 70,000 ha of gold tailings and sand dumps (Easton-Groves *et al.*, 1982). Although drought and acidity resulted in the early revegetation methods largely failing, over the last 30 years revegetation of gold mine residues has proved to be one of the more successful means of erosion control and pollution abatement in South Africa (Easton-Groves *et al.*, 1982).

The ameliorative approach is one frequently used to establish vegetation on mine wastes and refers to achieving 'optimum' plant growth conditions by improving the chemical and physical properties of the medium through the use of soil amendments which act to dilute and/or avoid toxicity (Johnson *et al.*, 1994). The remainder of this chapter discusses the potential benefits and problems associated with vegetative covers and reviews the use of lime and organic waste amendments and the metal-tolerant plant species for reclamation purposes.

3.7.1 Potential Beneficial Effects of Revegetation

Besides being useful for stabilising mine wastes against wind and water erosion, assisting in the immobilisation of potentially toxic cations and improving the aesthetic appearance of the site, vegetative covers may also serve to reduce the rate of biochemical sulphide oxidation (Ritcey, 1989). The potential benefits associated with the establishment of vegetative covers on metalliferous mine wastes are discussed below.

3.7.1.1 Stabilises Against Erosion

Land devoid of vegetation is much more vulnerable to erosion resulting from rainfall and wind (Verma & Thames, 1978). Thus one of the primary objectives of reclaiming mine-wastes is to stabilise them against wind and water erosion. Vegetative stabilisation is often the preferred method for the reclamation of both active and abandoned mine sites due to its potentially more permanent nature, its aesthetic value and because it usually allows for a wider range of end uses (Norland *et al.*, 1993).

In the United States, dust is considered to be a major environmental problem that affects land adjacent to inactive tailings ponds (Nielson & Peterson, 1978). Wind erosion of fine-grained tailings (<100 microns) may also exacerbate AMD by continually exposing previously unweathered material and thereby accelerating the rate of sulphide oxidation (Johnson *et al.*, 1977).

Plant organs provide effective protection from the physical effects of wind and water erosion both above and below-ground (Norland *et al.*, 1993). Below ground level, plants act to bind particles by firstly, physically holding the particles in place and secondly by encouraging the activity of soil organisms which promote soil aggregate formation. Physically, plant roots, root hairs and fungal hyphae bind particles together to form macro-aggregates. The growth and expansion of plant roots in the soil pores creates pressure on the proximal soil particles, physically holding them in place (McLaren & Cameron, 1990).

‘Soil’ stability is promoted biochemically by vegetation through the effects of organic matter accumulation in the soil medium. Organic matter promotes the activity of some 200 genera of bacteria and 170 genera of fungi that exist in the soil microbial community (Land Resources Network Ltd., 1993). Organic matter breakdown by saprophytic bacteria results in the production of mucilage or ‘glue-like’ compounds in the plant root rhizosphere. These organic compounds effectively glue soil particles together to form larger aggregates. Polysaccharides exuded by plant roots bind particles together in much the same way (Molloy, 1988).

Another mechanism by which soil stability is promoted is through the flocculating characteristics of polysaccharides and other long chain polymers such as humic and fulvic acids. These organic polymers are derived from the degradation of organic matter and carry net negative charge. This charge, combined with their flexible structure, enables polymers to effectively link soil colloids and assist soil aggregate formation (McLaren & Cameron, 1990).

Above ground, vegetation aids in the prevention of water erosion by reducing the impact of raindrops and by reducing the volume and velocity of surface run-off. Rill erosion (one of the most common forms of erosion affecting mine tailings) is readily eliminated by the introduction of an appropriate vegetative cover. The severity of wind erosion can also be abated by vegetation which reduces wind velocities at the 'soil' surface and also captures fugitive dust. In wind prone areas measures to revegetate the tailings often require steps being taken to prevent 'sand blasting' and/or burial of emerging seedlings. In South Africa this problem has been effectively dealt with by the use of dry reed windbreaks (Easton-Groves *et al.*, 1982).

3.7.1.2 Increases CEC and Specific Adsorption

Humus derived from the breakdown of accumulated organic matter is responsible for about 20% to 70% of the CEC of soils (Land Resources Network Ltd., 1993). The ability of humic substances to act as cation exchangers arises from the presence of functional groups such as ionisable carboxyl and phenolic hydroxyl carried on the organic polymers (McLaren & Cameron, 1990). These predominantly negatively charged functional groups act as exchange sites not only for cationic plant nutrients such as Ca^{2+} , K^+ and NH_4^+ , but also to some extent for potentially toxic non-essential metallic elements including Al^{3+} , Cd^{2+} and Pb^{2+} (Land Resources Network Ltd., 1993; Ritcey, 1989).

Although required by plants in small amounts, micronutrients such as Cu^{2+} , Mn^{2+} , Cu^{2+} and Zn^{2+} become toxic to plants if high concentrations are present in soil solution. These micronutrients, along with the non-essential metallic cations are bound to soils by specific adsorption and by simple cation exchange. Specific adsorption, however, is considered to dominate soil adsorption of polyvalent micronutrients and heavy metals and refers to the formation of stable complexes with specific functional groups at the surface of inorganic and organic soil colloids (McLaren & Cameron, 1990).

Cation exchange and specific adsorption are thus extremely important mechanisms in that they serve to simultaneously reduce the bioavailability and mobility of the toxic metal cations and increase a material's ability to retain plant nutrients which may otherwise be lost via leaching.

3.7.1.3 Reduces Oxygen Ingress

One of the primary variables that governs the rate at which oxidation occurs in sulphidic mine wastes is the availability of oxygen. In the case of fine grained wastes such as tailings, diffusion as opposed to convection is considered to be the primary mechanism of oxygen transport (James & Eng, c.1992). The depth to which oxygen diffuses into a material is dependent chiefly on its texture and on the oxygen consuming characteristics of the material. Thus, a considerable reduction in the contaminant load of drainage water emanating from sulphide-bearing wastes can, in theory, be achieved by minimising the rate of oxygen diffusion and/or by ensuring biological oxygen demand (BOD) is maximised within surface horizons.

The BOD of surface materials can be increased through the gradual accumulation of organic matter (via the establishment of a vegetative cover) or alternatively by the application of organic wastes (Pulford, 1991). Research indicates that as vegetation becomes established, soil organisms, decaying organic matter and plant roots deplete oxygen in the plant root zone (Ritcey, 1989; Pulford, 1991). As discussed in section 3.6.4.3, biological activity associated with the breakdown of organic matter thus effectively acts as a sink for atmospheric oxygen and dissolved oxygen in infiltrating water. The accumulation of organic matter in surface 'soil' horizons is therefore generally encouraged as a means of restricting the amount of oxygen available for the oxidation of sulphide minerals within underlying strata.

3.7.1.4 Decreases Leaching

As previously discussed, water plays an integral role in the oxidation of sulphide minerals and in the production of AMD. The ingress of water into tailings may be substantially reduced by vegetation which intercepts and returns rainfall to the atmosphere via evapotranspiration. Johnson *et al.*, (1994) suggest that in temperate climates, vegetation will intercept and return about 50% of the rainfall to the atmosphere. This is a very approximate figure only as the amount of incident rainfall returned to the atmosphere via evapotranspiration is highly dependent upon numerous site specific variables including the type of vegetation, climatic conditions and the nature of the rainfall.

3.7.1.5 Increases Plant Diversity

Improved physicochemical¹⁴ and biological properties afforded by organic matter accumulation associated with the establishment of vegetation on mine wastes can accelerate the development of a viable nutrient cycle and lead to a more diverse self-sustaining vegetative cover (Norland *et al.*, 1993; Winterhalder, 1995a, 1995b). Improving plant growth conditions will eventually enable less tolerant plant species to colonise once hostile growing media and in most cases will ultimately facilitate the growth of vegetation consistent with that hosted by surrounding land.

Research conducted near Sudbury, Canada, investigating the reclamation of extensive areas of acidified metal-contaminated land, found that the addition of dolomite and grass/legume seeds at rates of 10 Mg/ha and 45 kg/ha respectively, promoted colonisation of the area by native trees and herbaceous plants (Winterhalder, 1991). It was found that over time the relative abundance of sown grasses on seeded areas decreased, while sown legumes and native plant species increased.

3.7.1.6 Improves Site Aesthetics

Perhaps the greatest attribute of vegetative covers is their ability to improve the aesthetic appearance of denuded mine sites. Even simple grass covers can significantly reduce the obtrusive impact of tailings and waste rock dumps, however, the planting of shrubs and trees may be more useful for concealing the topography of engineered structures (Scheltus, 1990).

Many reclamation schemes aim at establishing vegetation that is consistent with the surrounding landscape. This aids in the creation of a cover that merges with the adjacent vegetation and minimises any negative visual impact of the site.

¹⁴ Refer to sections 3.7.4.1 & 3.7.4.2 for specific discussion.

It should be noted, however, that revegetative reclamation does not always aim at 'camouflaging' mined land (Boffa, 1990). In some instances reclamation is used as an opportunity to change the vegetative cover. Land revegetated with native bush, for example, can provide habitats for native flora and fauna and recreational areas for people living in deforested landscapes. Alternatively land mined within scrub may be reclaimed with improved pasture species to create highly productive pastures for grazing purposes.

3.7.2 Potential Negative Effects of Revegetation

Although the establishment of a vegetative cover on mine wastes is generally considered to be beneficial at least in terms of its aesthetic value, negative effects may potentially arise. Two such effects that can potentially exacerbate environmental degradation are the reductive dissolution of weathered compounds and increased sulphide oxidation arising from improved aeration and water infiltration.

3.7.2.1 Reductive Dissolution

As previously discussed, one of the primary benefits of establishing vegetation on mining wastes is that it introduces organic matter into the system. Some research suggests, however, that the build-up of humified organic matter in surface tailings either indirectly through the gradual decay of vegetation or directly via the application of sewage sludge or composted municipal waste, for example, may exacerbate acid mine drainage (Land Resources Network Ltd., 1993; Ribet *et al.*, 1995).

Treatments that induce reducing conditions may result in the release of potentially toxic metals (previously adsorbed or co-precipitated with ferric oxy-hydroxides) into surface and/or ground water (Ribet *et al.*, 1995). Research conducted at the Nickel Rim Mine located near Sudbury in Canada, found that more than 80 % of Fe, Ni, Cu and Co in the oxidised zone of tailings at the site were available for release by reductive dissolution (Ribet *et al.*, 1995). The mobility of metals released by reductive dissolution may be increased by specific adsorption of metallic cations by small, soluble organic polymers such as fulvic acid produced from decaying organic matter.

Increased metal loading of drainage water is not the only potential problem associated with reductive dissolution of metal compounds. Under oxidising conditions Fe^{2+} released into the water may oxidise and undergo hydrolysis to liberate acid. Thus, acidification of drainage waters can potentially occur.

3.7.2.2 Increases Oxygen & Water Ingress

As previously discussed¹⁵ vegetative covers can reduce the ingress of oxygen and water into materials via evapotranspiration and increased BOD respectively. The ability of planted surfaces to reduce the ingress of these substances may, however, be partially negated by improving 'soil' structure and macroporosity associated with accumulating organic matter and pedogenesis. Improved macroporosity and surface permeability may increase the ingress of oxygen and water into the surface horizons and potentially deeper into the profile to facilitate sulphide oxidation and the formation of AMD.

The interaction between increased permeability and evapotranspiration/BOD is clearly antagonistic in terms of AMD generation and will be dependent on the interplay of parameters such as the physical nature of the material, vegetation type, climate and nature of incident rainfall.

3.7.3 Lime Application

Neutralising agents such as limestone are the most commonly used amendments for aiding the establishment of vegetation upon sulphidic mine wastes (Pulford, 1991; Dollhopf, 1992). The rationale for the addition of limestone to ameliorate acidic conditions is as follows:- (i) the plant nutrient Ca is being added to the soil along with Mg if dolomitic limestone is used, (ii) mineral acidity is neutralised as well as acidity due to Al^{3+} , (iii) P availability may be increased, (iv) Fe oxidising bacteria are displaced due to unsuitable pH conditions and (v) exchangeable Al, Fe and Mn are greatly reduced, (Jackson, 1958; Smith & Sobek, 1978; Johnson *et al.*, 1994).

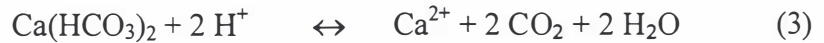
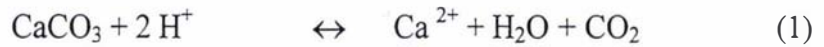
Maclean & Dekker (1976) found that for metalliferous tailings, providing sufficient limestone is applied to maintain the pH at circumneutral levels, heavy metal toxicity is

¹⁵ See sections 3.7.1.3 & 3.7.1.4

not generally a problem. This finding is in accordance with the recognised relationship between pH and metal solubility in soils (Mortvedt *et al.*, 1972; Alloway, 1995).

3.7.3.1 Acid Neutralisation

Acid is neutralised by limestone via one of two mechanisms. Under strong acid conditions limestone (CaCO_3) dissolves relatively rapidly to neutralise H^+ in solution (equation 1), whereas under weak acid or even neutral conditions the presence of carbon dioxide (CO_2) favours the dissolution of calcium CaCO_3 by forming calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$) which in turn neutralises solution H^+ (equations 2 & 3).



Although the liming of acid generating materials often enables plants to initially establish, plant die-back may occur if the liming agent is either consumed or incapable of reacting at a rate sufficiently rapid to neutralise acid released from sulphide oxidation. The second scenario may arise in situations where the grainsize of the limestone is too coarse (Gemmell, 1981; Costigan *et al.*, 1984), or alternatively when the limestone particles become armoured by weathering compounds (Costigan *et al.*, 1984; Evangelou, 1994). Plant die-back within a year or two of sowing, however, most commonly arises as a result of underestimating the liming requirement of pyritic wastes and applying insufficient limestone to maintain the pH at levels conducive to plant survival (Johnson *et al.*, 1977).

In situations where very high liming rates ($>100 \text{ Mg/ha}$) are required to neutralise acid and to prevent reacidification of growing media (via sulphide oxidation), potential problems can arise that can negatively impact plant growth. These problems include enzyme inactivation, induced Cu, B, Mg, Mn and P deficiencies and accelerated N loss through leaching (Doubleday 1972; MacLean & Dekker, 1976; Gemmell, 1977, Pulford, 1991). These problems are generally worst in materials that are poorly buffered and may in severe cases lead to total plant die-back.

Phosphorus is perhaps the most problematic of the macronutrients in terms of its availability in mining wastes. Not only is P generally deficient in such materials but its availability is highly dependent on pH. At low pH (<4), P is largely immobilised by anion adsorption by colloidal Fe and Al materials, whereas at high pH (>7) the formation of precipitates of low solubility phosphates becomes an important mechanism governing its availability. In heavily limed materials (or in calcareous soils) the formation of highly insoluble tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) often occurs which can fix P and render it largely unavailable for plant uptake. Research outlined by Mengel & Kirkby (1987) indicates that phosphate uptake by some species is 10 times greater at pH 4 than at pH 8.7. This difference is attributable to the fixation of P in the highly alkaline conditions and the faster uptake of H_2PO_4^- under the acidic conditions which favour the formation of primary orthophosphate.

Another widely recognised limitation of using limestone to neutralise acidity in growing media is that it is an ineffective means of ameliorating 'subsoil' acidity, due to the slow rate at which lime derived alkalinity leaches down the profile (Costigan *et al.*, 1981; Dollhopf, 1992). Thus, amendment incorporation is considered to be vital, particularly in highly acidic growing media. Research indicates that whilst standard agricultural discs, sub-soilers and moldboard ploughs can incorporate lime efficiently to depths of about 25 cm, tractor mounted rototillers probably provide the most efficient means of incorporating lime into mining wastes (Dollhopf, 1992).

Whilst the shear strength of waste rock materials is usually adequate to support the weight of wheeled vehicles for lime spreading and incorporation, low ground pressure machines (ie. tracked vehicles) may be required on poorly consolidated tailings or saturated materials.

3.7.4 Organic Waste Application

Soil organic matter has long been considered the "*elixir of plant life*" (Allison, 1973) and is well recognised as an important factor governing the versatility and productivity of agricultural soils under pasture and more specifically land disturbed by mining activity (Halderson & Zenz, 1978; Sopper, 1992). Numerous studies conducted over the

past 60 years have shown that amending soils with organic waste materials increases organic matter content and improves soil structure and long term fertility (Joost *et al.*, 1987). The effect of a variety of organic wastes including crop residues, farmyard manures, municipal composts and sewage sludges, lignite, peat, wood-wastes and papermill byproducts have been studied (Jozefaciuk *et al.*, 1990; Pulford, 1991). Specific examples pertaining to the application of such materials are outlined in an extensive review that summarises the use of organic materials as soil amendments in reclamation (Land Resources Network Ltd., 1993).

Sludge¹⁶ is one of the most commonly used organic amendments in land reclamation schemes around the world and literature pertaining to its use is readily found (Dinauer *et al.*, 1977; Gemmell, 1977; Johnson *et al.*, 1977; Halderson & Zenz, 1978; Seaker & Sopper, 1983, 1984, 1988a, 1988b; Crites, 1984; Atkinson *et al.*, 1991; Förstner, 1991; Moffat *et al.*, 1991; Sopper, 1992; Land Resources Network Ltd., 1993; Pichtel *et al.*, 1994). Although most of this research is centred on the use of sewage sludge in colliery spoil reclamation, much of the information contained in the literature is relevant to the reclamation of other mining wastes including base-metal tailings.

The disposal of sludge generated from sewage treatment plants is a serious problem facing numerous cities around the world (Sopper, 1992). Within the last few decades the problem has been exacerbated by growing populations and environmental lobbying. This has forced governing bodies to cease the dumping of sludge into river systems, lakes and oceans. In the USA it is estimated that more than 7.7 million tons of dry municipal sludge are produced each year by 15,300 treatment plants scattered throughout the country (Sopper, 1992). New Zealand produces about 52,000 tonnes of dry sewage per year (McLaren & Cameron, 1996). Because the sheer volume of sludge produced by sewage treatment plants makes the disposal of sludge by other methods (eg. incineration, land-fills) costly, land based disposal of sludge onto agricultural and degraded land is encouraged as it is considered to be both cost-effective and potentially beneficial to soils (Förstner, 1991).

¹⁶ For the purposes of this review 'sludge' is used as a generic term to describe any aerobically or anaerobically treated solid waste derived from municipal sewage treatment plants. The material is assumed to contain negligible quantities of pathogenic organisms.

Sludge application to organically impoverished soils and mining wastes is considered to be an effective means of recycling organic matter and essential plant nutrients removed from soils as a result of cropping and grazing practices (Smith, 1994). For these reasons some researchers suggest that sludge should be regarded as a resource rather than a waste product (Werner *et al.*, 1991; Sopper, 1992; Lottermoser & Morteani, 1993). The effects of sludge addition on the physical, chemical and biological characteristics of mine spoils are discussed below.

3.7.4.1 Beneficial Chemical Effects

A variety of 'soil' chemical parameters are known to potentially benefit from the addition of sludge. These include plant nutrient levels, cation exchange capacity (CEC), electrical conductivity, pH buffering capacity and soil reaction (Dinauer *et al.*, 1977).

(i) Nutrient Addition

The ability of sludges to supply large quantities of organically bound nutrients to 'soil' media is one of the most widely recognised benefits associated with its application. It is estimated that in the vicinity of 90% of the total N and S and between 10% and 50% of the total P exist in organic forms in soil surface horizons (Land Resources Network Ltd., 1993). Mineralisation facilitated by micro-organisms and soil fauna is responsible for transforming organically bound nutrients into compounds that are more readily available to plants (Land Resources Network Ltd., 1993). The enrichment of nutrients through sludge addition is particularly evident when used to amend mining wastes which commonly exhibit multiple nutrient deficiencies (Gemmell, 1977; Johnson *et al.*, 1994). Deficiencies of N and P in such wastes are often encountered and are potentially remedied by the addition of sludge which usually contains appreciable quantities of these macronutrients (Gilmour *et al.*, 1977; Olsen & Barber, 1977; Sopper, 1992).

In addition to N and P, sludges often contain variable quantities of Ca, K, Mg, S and a variety of other trace elements that may aid in the correction of nutrient deficiencies (Olsen & Barber, 1977; Sopper, 1992). There are numerous reviews and studies that specifically discuss the nutritional benefits of sewage sludge addition to both soils and mining wastes (Chaney & Giordano, 1977; Gilmour *et al.*, 1977; Olsen & Barber, 1977;

Sopper *et al.*, 1982; Topper & Sabey, 1986; Seaker & Sopper, 1988a/1988b; Jozefaciuk *et al.*, 1990; Atkinson *et al.*, 1991; Moffat *et al.*, 1991; Sopper, 1992; Pichtel *et al.*, 1994).

(ii) Increased CEC

As discussed in section 3.7.1.2, one of the key attributes of soil organic matter is its ability to exchange and electrostatically bind cations from the soil solution (Land Resources Network Ltd., 1993). A material's CEC is primarily controlled by its colloidal organic matter and clay mineral content and is a very important parameter in that it governs the availability of nutrient cations and essential and non-essential 'trace' elements (Keeney & Wildung, 1977; Sopper, 1992). Since organic amendments, such as sludge, usually have high CEC their addition generally increases a substrate's ability to retain cationic plant nutrients including NH_4^+ , Ca^{2+} , K^+ , Mg^{2+} , Mn^{2+} , Fe^{2+} , Cu^{2+} and Zn^{2+} (Land Resources Network Ltd., 1993).

The humus component of organic matter is largely responsible for CEC due to its comparatively high surface area per unit mass and hence more chemically reactive functional groups. Since the charge exhibited by humus is largely generated by the presence of carboxylic, phenolic and hydroxyl functional groups, the CEC of such materials tends to increase with pH (Land Resources Network Ltd., 1993). In acid soils Ca^{2+} , K^+ , Mg^{2+} , Al^{3+} and $\text{Al}[\text{OH}]^{2+}$ generally dominate the exchange complex, whereas in calcareous soils Ca^{2+} and Mg^{2+} occupy most of the exchange sites (Keeney & Wildung, 1977). The benefits of adding sludge in terms of CEC is therefore largely dependent on the pH of the amended substrate and the quantities of colloidal organic matter present in the sludge. Non-composted or 'fresh' sludge with a low humic colloid content is, therefore, less likely to ameliorate a substrate's CEC in the short term. Humification of the organic matter is, however, likely to improve CEC with time.

(iii) Moderated pH

The increase in CEC afforded by organic matter addition, not only improves the retention of nutrients and non-essential metal cations, but also serves to buffer pH change via the release and absorption of hydrogen (H^+) and aluminium (Al^{3+}) ions from the exchange sites. The pH buffering capacity of a soil is largely governed by CEC and

the degree of saturation of the exchange complex with Al^{3+} and H^+ (often termed reserve acidity; Keeney & Wildung, 1977). Thus, soils with higher CEC tend to be more resistant to changes in pH than soils with lower CEC.

Although pH buffering is known to reduce extreme acidity in mining wastes, the pH of such wastes is also ameliorated due to the liming action of sludge materials. Sludges with near neutral to alkaline pH can raise the pH of acidic mine wastes substantially by simple dilution. In one notable study, Sopper & Seaker (1990) found that the addition of sludge at a rate of 184 Mg/ha increased the pH of colliery spoil from 3.8 to 6.2 within four months of application. Twelve years later, the pH of the substrate was still found to be comparatively high (5.4). Several studies outlined by Sopper (1992) indicate that sludge may be more effective at maintaining pH levels than limestone despite it having a substantially lower calcium carbonate equivalency. Joost *et al.*, (1981), for example, reported that the application of sludge at rates of between 450 and 900 Mg/ha maintained pH for a longer period of time than limestone applied at a rate of 180 Mg/ha.

Sludge has also been used to ameliorate the pH of highly alkaline substrates (Topper & Sabey, 1986). pH buffering involving the liberation of acidic cations from the exchange sites is believed to be largely responsible for alkaline 'neutralisation' in such situations. Sopper (1992) outlines research, however, which indicates that increased infiltration resulting from the addition of sludge may facilitate leaching of alkaline compounds from surface horizons.

(iv) Heavy Metal Attenuation

Sludge addition generally serves to lower the bioavailability of non-essential metals via mechanisms including cation exchange, specific sorption, chelation, precipitation and complexation with phosphates and hydrous oxides (Chaney & Giordano, 1977; Corey *et al.*, 1981; Hinkle, 1982; Seaker & Sopper, 1983/1984; Sopper, 1992). Chaney (1973) regarded organic matter chelation along with CEC as the most important factors controlling metal availability. Precipitation and other forms of specific adsorption processes involving covalent bonding to certain functional groups on clay colloids is also believed to dominate in some soils (Keeney & Wildung, 1977).

Whereas single charged cations are held mainly by simple cation exchange, multi-charged cations such as Cu^{2+} , Mn^{2+} and Zn^{2+} tend to form complex chelation linkages with organic matter (Stevenson, 1982). Keeney & Wildung (1977) describe chelation as a form of complexation that occurs between metal ions and organic ligands and results in the “*the formation of a heterocyclic ring which includes the metal ion*”. Chelates tend to form more stable complexes than analogous complexes in which the metal is coordinated in a non-cyclic fashions with water, other ligands or both (Keeney & Wildung, 1977).

Regardless of its precise nature, organo-metal complexation is known to play a significant role in decreasing free-metal activity and often serves to palliate phytotoxicity in heavy metal contaminated substrates (Chaney & Giordano, 1977; Förstner, 1991; Alloway, 1995). Elliot *et al.* (1986) found that in terms of metal retention the addition of organic matter to growing media was generally most effective under acidic conditions where secondary metal sulphates, carbonates, oxides and hydroxides are unstable. Keeney & Wildung (1977) provide a useful review of the various soils processes and mechanisms that are involved in the fixation and exchange of metals and plant nutrients.

3.7.4.2 Beneficial Physical Effects

The potential physical benefits of adding sludge to mining wastes such as the Tui mine tailings are numerous and well documented. Soil physical parameters potentially improved by the incorporation of sludge include; bulk density, water holding capacity, particle aggregation (stability), soil porosity and aeration, hydraulic and thermal conductivity and surface water infiltration (Sopper, 1992; Land Resources Network Ltd., 1993). The combined effects of incorporating sludge is often manifested in a substrate that is more resistant to wind and water erosion and has improved structure, aeration and water holding capacity. Clearly such improvements in the physical nature of a substrate would benefit seed germination and the subsequent establishment of plants.

Sopper (1992) and Land Resources Network Ltd. (1993) outlined several studies in which the benefits of sludge addition were shown to greatly improve the physical condition of various sludge amended substrates. Because greatest yield improvements are often observed when organic matter levels in sandy or clayey substrates are increased (Land Resources Network Ltd., 1993),

(i) Bulk Density

The degree to which sludge addition reduces the bulk density of a given substrate is proportional to the amount of sludge added and is dependent on the relative bulk densities of the materials (Metzger & Yaron, 1987). Because most types of sludge have comparatively much lower bulk densities than mining wastes, the addition of sludge to such materials invariably reduces the bulk density via simple dilution. The introduction of organic matter may, however, also indirectly reduce the bulk density by facilitating the establishment of soil organisms that serve to aggregate soil particles and to aerate and improve the structural integrity of the substrate (Land Resources Network Ltd., 1993).

(ii) Aggregation & Porosity

As discussed in section 3.7.1.1 several factors associated with the addition of organic matter assist soil aggregate formation. Joost *et al.* (1987) reported that applications of high rates of sewage sludge (225-900 Mg/ha) reduced the bulk density of acid colliery spoil and increased the number of water-stable aggregates and the proportion of macropores present in the amended spoil. Land Resources Network Ltd. (1993) cites several studies in which similar results were found.

Although some research findings suggest that sludge improves the overall porosity of soils, there are conflicting findings regarding the ability of sludges to improve macroporosity (Pagliai *et al.*, 1981; Wei *et al.*, 1985). Obviously the effects of sludge on macroporosity would depend heavily upon the initial condition of the 'soil' and upon the biological and physical nature of the sludge and the rates applied.

(iii) Hydraulic Conductivity

In addition to its ability to ameliorate bulk density and porosity, several studies indicate sludge application can substantially improve water infiltration and saturated hydraulic conductivity (Sopper, 1992). Some research indicates that the presence of organic matter at the 'soil' surface aids infiltration by preventing crusting (Pagliai *et al.*, 1983). Clearly any increase in macroporosity is likely to result in increased infiltration and higher hydraulic conductivity. Improved infiltration arising from the application of sludge has been shown to reduce run-off, erosion and sedimentation from mine spoils (Sutton & Vimmerstedt, 1974).

Based on the preceding discussion (section 3.7.4.2) it is clear that the physical parameters effected by sludge addition are highly inter-related and that sludge addition is likely to improve several soil parameters simultaneously.

3.7.4.3 Biological Effects

The impact and role that soil micro-organisms play in recycling, fixing and liberating nutrients is perhaps the most poorly understood aspects of land reclamation by practitioners. Many practitioners fail to fully appreciate the complex and interactive role that soil microbial populations play in breaking down organic matter and regulating the chemical and physical fertility of a soil. A 'typical' soil contains a vast number and variety of micro-organisms including bacteria, fungi, algae actinomycetes and protozoa (Ritcey, 1989, Land Resources Network Ltd., 1993). Thus if the ultimate long term objective of a reclamation program is to create a self-sustaining soil ecosystem that is capable of hosting a variety of plants and fauna, an integral part of achieving such a goal will be to ensure that the soil contains a functional microbial population (Sopper, 1990).

Although the composition of microbial populations is highly dependent on the micro-environmental conditions prevailing in a soil medium, the majority of organisms in substrates containing organic matter are heterotrophic saprophytes which gain their energy source from carbon. In substrates that contain negligible organic matter, heterotrophic organisms are largely absent. Instead chemo-autotrophic organisms which gain their energy from inorganic chemical compounds are likely to be predominant. The

integral role that chemo-autotrophs such as *Thiobacillus ferrooxidans* play in the oxidation of sulphide minerals is discussed in section 3.3.1.

Sludge addition to sulphide bearing wastes is likely to adversely affect the stability of chemo-autotrophic bacterial populations due to increased pH and the presence of organic compounds that favour the growth of heterotrophic bacteria (Brown *et al.*, 1990). The addition of heterotrophic bacteria capable of breaking down organic matter to release stored macronutrients (chiefly N & P) into the soil solution is also likely to ameliorate growing conditions in amended substrates (Seaker & Sopper, 1988a). Many of the microbiological processes that govern the availability of individual nutrients, however, are highly complex and involve a multitude of micro-organisms. In the nitrogen cycle for example, the processes of fixation, nitrification, denitrification, mineralisation and immobilisation are all governed by soil microbes (Ritcey, 1989; Sopper, 1992). All of the above processes are totally dependent on the presence of at least one specific bacterial population and will not take place unless the bacteria are present and the environmental conditions are suitable (eg. *Rhizobial* fixation of nitrogen). Since some bacteria are more sensitive to adverse growing conditions than others, specific nutrient deficiencies may arise as nutrient cycling processes that are catalysed or facilitated by bacteria are inhibited. At high concentrations metals such as Cd, Cr, Cu, Pb and Zn may interfere with microbial function and have been shown to inhibit soil bacterial and fungal activity (Babich & Stotsky, 1977).

Although sludge application to agricultural soils has been shown to decrease microbial biomass due to metal toxicity (Brookes & McGrath, 1984), the application of sludge to mine wastes is generally beneficial in that it increases the diversity and activity of soil micro-organisms. Most of the studies that have investigated the impact of organic wastes on the microbiological populations of mining wastes have indicated that sludge addition invariably enhanced microbial activity (Fresquez & Lindemann, 1982; Visser *et al.*, 1983; Stroo & Jenks, 1985; Fresquez & Aldon, 1986; Seaker & Sopper, 1988a; Smith, 1991; Hetrick *et al.*, 1994; Shetty *et al.*, 1994).

3.7.4.4 Effects of Sludge Addition on Plant Yield

Sopper (1992) reviewed several studies in which the combined effects of sludge addition on soils and mining wastes were manifested by improved plant growth yields. In general, the studies demonstrated that good plant cover can be established on many types of disturbed land using municipal sludge. Differences in substrate composition and climate were, however, found to significantly influence the performance of plants species. For example, whilst tall fescue (*Festuca arundinacea*) was found to perform well in a study investigating the addition of sludge to highly acidic strip-mine spoil (Sopper & Kerr, 1982), it completely failed when used on soils contaminated by zinc (Franks *et al.*, 1982).

Research evaluating the use of composted sewage sludge/straw on three contrasting derelict sites in the UK, found that there was a linear relationship between plant yield and composted sewage sludge/straw applied (Atkinson *et al.*, 1991). The increased yield was attributed to an improvement in the nutrient status and physical properties of the spoils. Another study looking at the use of sewage sludge in the amendment of coal spoils (Moffat *et al.*, 1991) found that the addition of sludge increased tree and ground cover growth. Dramatic increases in foliar N and P were also noted.

3.7.4.5 Problems associated with Sludge Application

Detrimental agronomic and environmental problems can arise with the use of organic amendments. Problems associated with the inappropriate use of organic amendments such as sewage sludge include:- (1) Induced nutrient deficiencies (N, P and S) can arise in materials containing extremely high C levels. (2) Surface run-off of applied waste and/or the leaching of soluble salts (eg. nitrate) from organic wastes can pollute water ways and potentially result in eutrophication. The latter problem of nitrate leaching is usually most severe in situations where the sludge is applied in liquid form. (3) The addition of organic materials to poorly drained substrates can lead to nitrogen loss via biological denitrification. The generation of gaseous compounds such as nitrous oxide via denitrification not only reduces the nutrient content of the amendment but can contribute to ozone depletion and global warming. (4) Some wastes, particularly sludges sourced from industrial areas, contain elevated concentrations of heavy metals and persistent organic toxins. These contaminants may accumulate in soils and be

introduced into the human food chain by crop or stock uptake, or by the contamination of potable water. (5) In metalliferous wastes organic matter treatments can cause reductive dissolution of heavy metals previously adsorbed or co-precipitated with the iron oxy-hydroxides. This process can ultimately result in the release of potentially toxic metals compounds into surface and ground water (Sopper, 1992; Land Resources Network Ltd., 1993; Ribet *et al.*, 1995).

(i) Heavy Metal Contamination

The most widely publicised and studied of the potential hazards associated with the use of sludge amendments is that of metal contamination. Sludges often contain appreciable concentrations of metals including Cd, Cr, Cu, Mo, Mn, Ni, Pb and Zn (Förstner, 1991). Cu, Mo, Ni, Zn and particularly Cd tend to be the most problematic of these metals in terms of their tendency to inhibit microbial activity and to threaten livestock and human food chains where the soils are used for cropping or grazing.

The interaction of sludge on the dietary uptake of metals such as Cd and Zn have been the focus of numerous studies (Alloway, 1977; Dean & Suess, 1985; Alloway, 1995; Sopper, 1992; Smith, 1994). A working group organised by the World Health Organisation identified Cd as one of the most potentially hazardous contaminants in sludges due to its ability to accumulate in certain crops grown on sludge amended soils (Sopper, 1992). Fortunately the translocation of most heavy metals into the human food chain is governed to a large degree by phytotoxicity which often results in crop failure in heavily contaminated plant growth media. There is a serious risk, however, of metals entering the food chain via ingestion of sludge amended soils along with forage (US EPA, 1983).

It is necessary to note that specific adsorption associated with sludge addition does not always result in the net immobilisation of metals within the root zone. As mentioned in section 3.7.2.1, the chelation of metals with smaller organic molecules, such as fulvic acid, can result in the formation of small highly soluble complexes (Land Resources Network Ltd., 1993; Ribet *et al.*, 1995). The mobility of small metal-chelates renders them susceptible to plant uptake and/or leaching from the 'regolith'. Where excessive

concentrations of metal chelates are present in root zone, phytotoxicity is likely to ensue.

Most of the US guidelines relating to the use of sludge are for agricultural soils and are based on trace metal loading and/or vegetation nutrient requirements (Sopper, 1992). Although no federal guidelines have been issued specifically governing the use of sludge for mine reclamation purposes, some states have developed stringent guidelines concerning the use of sewage sludge in such circumstances (Sopper, 1992). The Pennsylvanian Department of Environmental Resources, for example, limits sludge application rates based on crop nitrogen requirements and on the trace metal content of the sludge. Metal loading rates for reclaimed land in Pennsylvania are presented in Table 3.2. In Pennsylvania and other states, additional site and soil parameters such as topography, pH and CEC are employed to further reduce the environmental risks associated with the use of sludge. The New Zealand Department of Health (DOH) have issued similar guidelines based on soil pH and metal loading (DOH, 1992). The DOH guidelines include the following controls:- (i) the soil to which the sludge is being applied must have a pH of 5 or greater, (ii) the maximum concentrations of heavy metals in the surface 200mm of arable soils must not exceed those values presented in Table 3.2 and (iii) the maximum annual rates at which heavy metals contained in sludge can be applied to land must not exceed the bracketed values presented in Table 3.2 (McLaren & Cameron, 1996). Furthermore the DOH guidelines require that pH and heavy metal loadings are monitored on a 3 yearly and 5 yearly basis respectively.

Clearly the ethical dilemma of using metal-contaminated sludge as a 'soil' amendment is greatly reduced when the substrate itself contains comparable or higher concentrations of the 'contaminant'.

Table 3.2 Maximum recommended cumulative loading rates and maximum permitted total concentrations of heavy metals in sludge amended soils. Bracketed data represents the maximum recommended annual loading rate of heavy metal. * = Pennsylvania Department of Environmental Resources (Sopper, 1992).
^φ = New Zealand Department of Health Guidelines (DOH, 1992).

Constituent	Maximum Cumulative Loading Rate [kg/ha]		Maximum Soil Concentration [mg/kg]	
	Pennsylvania*		New Zealand ^φ	
	Not Farmed	Farmed		New Zealand ^φ
As	-	-	2.5 (0.2)	10
Cd	5.6	3.4	2.5 (0.2)	3
Cr	560	336	125 (15)	600
Cu	140	84	100 (12)	140
Pb	560	336	125 (15)	300
Hg	1.7	1.1	1 (0.1)	1
Ni	56	33	20 (3)	35
Zn	280	168	250 (30)	300

(ii) Pesticides

In addition to heavy metals, sludges often contain elevated levels of persistent organic compounds such as PCBs (polychlorinated biphenyls) and organochlorine pesticides. Like cadmium these contaminants are also of particular concern due to their longevity and tendency to find their way into the human food chain from sludge amended soils (McCalla *et al.*, 1977; Förstner, 1991). Fortunately evidence indicates that these compounds are not generally translocated to plants in high concentrations from heavily contaminated substrates. Root crops may, however, be more susceptible to contamination due to their propensity to uptake lipophilic substances (Förstner, 1991).

(iii) Nutrient Immobilisation

As alluded to above, N, P and S can be immobilised by the application of amendments which contain disproportionately high levels of carbon, or alternatively when the carbon contained is in a form such as lignin¹⁷ that is highly resistant to mineralisation. The latter scenario effectively lowers the C:N, C:P or C:S ratios. When these ratios exceed 30:1, 300:1 and 300:1 respectively, net nutrient immobilisation may occur due to the removal of plant available inorganic forms of N, P and S from the soil solution by

¹⁷ Lignin is a complex polymer that binds to cellulose fibres and hardens and strengthens the cell walls of plants.

microbes (Land Resources Network Ltd., 1993). The immobilisation of macronutrients via this mechanism is more commonly associated with the application of wood-waste amendments (Land Resources Network Ltd., 1993). Specific nutrient balances that do occur in sludge amended soils are usually rectified by the addition of inorganic fertilisers.

(iv) Application Rates & Frequency

Whilst discussing the limitations and potential risks involved with the use of organic amendments it is important to note that many of the beneficial effects of organic amendments are temporary in nature. Although few studies have exceeded 5 years it is apparent that without repeated applications and/or the presence of an established vegetative cover the initial improvements afforded by sludge amendment may rapidly disappear (Land Resources Network Ltd., 1993). Microbial degradation and soil forming processes, such as humification and leaching, may eventually exhaust organic matter and nutrient reserves which commonly take up to 30 years to establish on vegetated mine spoils (Sopper, 1992). In an investigation looking at the effects of sludge on sandy soils, Tester (1990) found that within 4 years of sludge addition over 50% of the organic matter had decomposed. Providing that at least part of the organic carbon is resistant to degradation, however, some of the beneficial effects of sludge addition are likely to persist (Metzger & Yaron, 1987). The establishment of plants on an amended substrate is considered to be the best way of ensuring soil organic matter level is maintained continuously through recycling (Sopper, 1992; Land Resources Network Ltd., 1993).

On reviewing the literature it was evident that although numerous studies have been conducted investigating the physical, chemical and biological effects of sludge addition to acid strip mine spoils (Sopper, 1992), published literature that specifically discusses the use of sludge in the reclamation of metalliferous wastes is relatively scarce (Johnson *et al.*, 1977; Gemmell, 1977; Hinkle, 1982; Wong & Lai, 1982; Morrison & Hardell, 1982; Ritcey, 1989; Borgegård & Rydin, 1989; Johnson *et al.*, 1994). Where high rates of sludge have been used to reclaim metalliferous wastes (including tailings) improvements in vegetation establishment have been attributed to improved water-

holding capacity, nutrient status and attenuation of heavy metals (Sopper, 1992; Land Resources Network Ltd., 1993).

3.7.5 Metal Tolerant Plant Species

A combined grass and legume cover is one of the most common components of land reclamation schemes due to the potential ability of this type of vegetative cover to grow rapidly and to produce a continuous, dense sward within a few months of sowing (Bradshaw & Chadwick, 1980). Legumes such as white clover (*Trifolium repens*) and birdsfoot trefoil (*Lotus corniculatus*) are considered essential components of swards established on substrates of low nutrient status because they contribute N to the growing medium by way of symbiotic rhizobial fixation and via mineralisation (Johnson *et al.*, 1977). Leguminous plants can contribute over 100 kg N/ha annually on well established pasture (Chadwick & Bradshaw, 1980) and are thus desirable in that they help establish a self-sustaining ecosystem by reducing or eliminating the need for supplementary nitrogen application after initial treatment.

Unfortunately, direct seeding with conventional legume and grass pasture species in conjunction with fertiliser addition is often unsuccessful on mine sites where high levels of acidity and heavy metals are encountered (Johnson *et al.*, 1994). Because direct seeding is economically a very attractive option in principle, considerable research was conducted in the United Kingdom (UK) investigating plant species that demonstrated a natural ability to tolerate high concentrations of heavy metals in the growth medium.

The phenomenon of metal tolerance in plants is believed to develop through genetic variation evolving from the proximity of non-tolerant plants to sources of contamination (Bradshaw & McNeilly, 1981). Metal tolerance in higher plants has been reported for various metals including As, Cd, Cu, Ni, Pb and Zn (Johnson *et al.*, 1994). Out-breeding plants such as those listed in Table 3.3 are more likely to evolve metal-tolerant ecotypes due to their greater natural variation and tendency to differentiate into local populations (Bradshaw & McNeilly, 1981; Gemmell, 1977). The extreme speed at which metal-tolerant grass populations can evolve was highlighted by a study conducted at a copper refinery situated near Prescott in the UK (Bradshaw & McNeilly, 1981). At this site

certain cultivars of *Agrostis stolonifera* were found to develop copper tolerance in less than 70 years and potentially in as few as four years on heavily contaminated soils.

Although observations of metal-tolerant flora date back to the 16th Century (Brooks, 1995), Bradshaw (1952) was amongst the first researchers to fully appreciate the application of such tolerance to the reclamation of metal contaminated mine-sites (Gemmell, 1977). Since Bradshaw's (1952) pioneering discovery of metal-tolerant varieties of *Agrostis capillaris*, over fifty species of plants capable of evolving metal-tolerant ecotypes have been identified (Antonovics *et al.*, 1971; Eslick, 1995). Some of these ecotypes hyperaccumulate metals and can survive the uptake of specific metals in concentrations well in excess of 10,000 mg/kg (Johnson & Proctor, 1977; Brooks, 1987; Baker *et al.*, 1988.)

In the UK the use of metal-tolerant grass populations in mine-site reclamation is well established and widely accepted as a potentially rapid and economical way of revegetating and stabilising materials that are phytotoxic to conventional plant species (Gemmell, 1977; Johnson *et al.*, 1977; Bradshaw, 1979; Bradshaw & Chadwick, 1980; Bradshaw & McNeilly, 1981). Many of the successful revegetation schemes in the UK involved the direct sowing of metal-tolerant cultivars of *Festuca rubra* and *Agrostis capillaris* that were isolated and cultured in a breeding program initiated during the 1970's. *A.capillaris* cv. Parys Mountain and Goginan were developed for acidic sites contaminated with copper and lead/zinc respectively. *F.rubra* cv. Merlin was isolated and bred specifically for use in the reclamation of lead and zinc-contaminated calcareous materials. There are a multitude of references specific to the use of these cultivars throughout the literature pertaining to the reclamation of surface mined lands (Chadwick, 1973; Darmer, 1973; Johnson *et al.*, 1977; Smith & Bradshaw, 1979; Bradshaw & McNeilly, 1981; Wong, 1982; Sudhakar *et al.*, 1992; Whitely & Williams, 1993, Johnson *et al.*, 1994). Although several studies including those of Day & Ludeke (1981), Wu & Lin (1990) and Sudhakar *et al.*, (1992) have concentrated on finding legume species suitable for revegetating metal contaminated sites, no species have yet been commercially developed. Although legume species display varying degrees of tolerance, the evolution of metal tolerance in legumes is considered to be a more

complex matter than that in non-leguminous plants and is clearly a less common phenomenon (Wu & Lin, 1990).

The commercially available metal-tolerant cultivars of *A.capillaris* and *F.rubra* are suited to temperate climates and can be classified as either elective or indifferent pseudometallophytes (Antonovics *et al.*, 1971). Pseudometallophytes differ from strict metallophytes in that they are capable of growing on both contaminated and non-contaminated soils. For the purposes of this study the term ‘metal-tolerant’ will be used to describe pseudometallophytic cultivars that have evolved the ability to withstand much greater concentrations of one or more heavy metals than cultivars of the same species established on non-contaminated soils.

Table 3.3 Selected grasses that have ecotypes exhibiting tolerance to metals found in non-ferrous metal mine spoils (Gemmell, 1977; Eslick, 1995).

Plant Species	Metal Tolerance
<i>Agrostis capillaris</i>	Zn, Cu, Pb, Ni
<i>Agrostis stolonifera</i>	Zn, Cu, Pb, Ni
<i>Festuca rubra</i>	Zn, Pb, Cu
<i>Festuca ovina</i>	Zn, Pb
<i>Agrostis canina</i>	Zn
<i>Anthoxanthum odoratum</i>	Zn

3.7.5.1 Limitations of Metal Tolerance

Although the overalls cost associated with the use of metal-tolerant plant varieties in mine-site reclamation are generally low, there are some major limitations preventing the use of metal-tolerant plants at all sites. The most obvious constraint is that some substrates are simply too ‘hostile’ to host even the most metal-tolerant plant taxa. Although some cultivars (eg. *A.capillaris* cv. Goginan) are calcifuges, most cultivars struggle to survive below pH values of about 4 where very high levels of metals generally start to enter the soil solution. In acidic conditions the tolerance mechanisms at work within the root system and shoots are generally quickly overwhelmed and multiple metal toxicity is likely to occur. This effect is compounded by the fact that metal tolerance is generally metal specific. Where cross-tolerance does occur (eg

F.rubra cv. Merlin, Pb/Zn) the metals are closely related and the secondary tolerance is generally low. Thus a particular cultivar is unlikely to survive on mine-wastes containing toxic quantities of metals other than those to which it has evolved tolerance or in circumstances where increased acidity increases the solubility of several metals simultaneously (Johnson *et al.*, 1994).

Another limitation associated with the use of tolerant species is that although they generally take up lower concentrations of metals than non-tolerant species, tolerant herbage obtained from toxic sites still usually contains excessive concentrations of biotoxic metals that may render it unsuitable for grazing by domestic animals. Dry matter concentrations of Pb, for example, are generally lethal to livestock when they exceed 100 mg/kg (Johnson *et al.*, 1977). The agricultural potential of such swards is therefore very limited. The toxicity of the pasture is also dependent on other factors including the combination of metals present, the species, age and condition of the livestock and the proportion of the diet comprising the contaminated vegetation (Antonovics *et al.*, 1971; Johnson *et al.*, 1977).

Substrates vegetated with metal-tolerant swards may also be unsuitable for recreation or amenity purposes due to the inability of some metal-tolerant swards to withstand heavy trafficking (Johnson *et al.*, 1994). Regardless of land use, successful establishment of a 'permanent' pasture is likely to require relatively heavy inputs of maintenance fertilisers and lime to maintain N and P macronutrient levels in particular (Bradshaw & Chadwick, 1980).

3.7.5.2 Mechanisms of Metal tolerance

Although a great deal of research has been undertaken investigating the impact of various heavy metals on plant germination and growth, comparatively little research has focused on the physiology of tolerant plants or the mechanisms by which they tolerate metals (Bradshaw & McNeilly, 1981). The several mechanisms which are believed to give rise to metal tolerance in plants can be divided into two categories, *exclusion* mechanisms which prevent toxic elements from entering sensitive plant tissues and *tolerance* mechanisms which involve the conversion of potentially toxic metals inside cells to 'inert' compounds (Baker *et al.*, 1988).

The ability of plants to selectively absorb metals and root cell-walls to bind metals, influenced early researchers to believe that exclusion mechanisms were largely responsible for governing plant tolerance. Very high lead uptake, for example, can occur under acidic conditions with comparatively little impact on the vigour of plants. It is believed that lead taken up in such circumstances is quickly inactivated through the precipitation of compounds such as lead phosphates on root surfaces, in extracellular spaces and within dictyosome vesicles of root cells (Foy *et al.*, 1978). This and similar exclusion mechanisms that possibly involve the excretion of plant-synthesised metal chelates into the rhizosphere are known to influence metal movement to sensitive shoot tissues (Alloway, 1995). Exclusion mechanisms (particularly in the case of tolerant plants) are partially responsible for the comparatively lower levels of metals that are generally found in the shoots of plants (Bradshaw & McNeilly, 1981).

Although the mechanisms that complex metals within the root and at the soil-root interface may contribute to metal tolerance, they do not prevent the accumulation of heavy metals in shoot material and fail to explain the ability of tolerant plants to withstand concentrations of heavy metals that are phytotoxic to the vast majority of other taxa (Foy *et al.*, 1978; Bradshaw & McNeilly, 1981). Research indicates that those metals that are not excluded from plant tissues may be bound in the cytoplasm by specific compounds produced by the plants (Bradshaw & McNeilly, 1981; Thurman & Hardwick, 1988). The observed accumulation of zinc in vacuoles of zinc tolerant grasses indicates that once bound the metal complexes may migrate from the cytoplasm to the inside of vacuoles where they can be 'safely' stored. Candidates for the binding role in the vacuole include organic acids and sugar phosphates. In the cytoplasm, likely binders are phytochelatins which are known to bind metals via cysteinyl residues (Thurman & Hardwick, 1988). Alternative mechanisms that may contribute to tolerance are the alteration of metabolic pathways within plants to prevent the translocation of specific metals to sensitive sites and/or the utilisation of toxic metals in physiological processes. The release of toxic ions from plants via foliar leaching, guttation, leaf shedding and root excretion may also contribute to tolerance in some species (Foy *et al.*, 1978; Alloway, 1995).

One finding on which there is widespread consensus is that there appears to be no single mechanism that is responsible for metal tolerance in higher plants. Rather, tolerance is believed to result from the interaction of several different mechanisms that may work independently or simultaneously in plant organs both above and below ground-level (Foy *et al.*, 1978; Bradshaw & McNeilly, 1981; Alloway, 1995). Because the mechanisms are believed to vary from species to species and are generally metal specific (and possibly even site specific) the genetic basis of tolerance is believed to involve a large number of genes.

3.8 Chapter 3 Summary & Conclusions

- From this literature review it is evident that environmental degradation is an inherent feature of some current mining operations and is often severe at many abandoned mine sites throughout the world. The magnitude of environmental impact resulting from mining activity is highly variable and depends on the type of mining and on the physicochemical nature of waste materials generated at mine sites.
- Whilst every mine site has a unique combination of environmental, physical and geochemical parameters, a common factor noted at many severely degraded sites, including the Tui mine site, is the presence of sulphide-bearing materials that have been exposed by mining activity and the lack of any rational reclamation plan.
- The oxidation of acid generating sulphide minerals results in the liberation of acidity (H^+), sulphate and metal cations. Sulphide minerals found in finely-ground mine tailings are generally highly susceptible to biochemical oxidation due to their relatively large surface area.
- Under certain environmental conditions some sulphide-bearing materials, which contain low concentrations of acid-neutralising carbonate minerals, generate Acid Mine Drainage (AMD) which can contaminate ground and surface water. Such drainages are characterised by their extremely low pH and high sulphate and metal contents and occur at the Tui mine site.
- Whilst direct physical degradation associated with mining activity, such as forest clearance, the displacement and/or burial of soils and the disruption of natural surface and subsurface drainage systems, may be severe, this type of degradation is generally localised. At mining sites where sulphide-bearing materials are prevalent and AMD

generation is established, however, the environmental impact can be much more widespread as contaminants are effectively mobilised by drainage water into the aquatic environment and from there potentially into the human food chain.

- The literature indicates that a wide range of active and passive treatment systems have been developed to treat AMD. Highly degraded, metal-contaminated drainage can be effectively treated via the addition of chemical additives, however, the costs of such active treatment systems are potentially very high and ongoing.
- Recent development of passive water treatment systems, which exploit natural processes to precipitate and/or complex soluble metals released during oxidation, have shown very promising results in the US where they are currently being extensively trialed.
- Mine reclamation techniques employed at abandoned mine sites generally aim at reducing environmental impact of past mining by:- (i) physically and chemically stabilising materials against erosion and chemical degradation and (ii) reducing the visual impact of disturbed lands. These objectives are most frequently achieved via the use of capping materials and/or the establishment of surface vegetation. At sites where sulphidic materials are encountered, the combined use of impervious caps and vegetation is not only designed to improve the physical stability and aesthetic appearance of the site but also to inhibit sulphide oxidation by restricting the ingress of oxygen and water into the sulphidic material.
- At mine sites where soil material is scarce, mining wastes are often used to create a 'surrogate soil' to host vegetation. Such materials are generally selected on the basis of their physical and chemical merits but are, almost always, deficient in organic matter and plant nutrients. Low pH and the high bioavailability of phytotoxic metals are additional problems commonly associated with sulphide-bearing materials.
- Although metal-tolerant plants have been used successfully and extensively at mine sites in the UK to revegetate sulphide-bearing mine wastes, these materials still generally require nutrient addition and pH adjustment to facilitate the growth of these plants.
- Nutrients may be added via the application of inorganic fertiliser or, alternatively, by the incorporation of nutrient-rich organic wastes. Composted sewage sludge is a particularly useful amendment for mine wastes in that it not only provides a valuable source of plant nutrients and organic matter for metal adsorption but also because it

improves a variety of 'soil' physical properties such as bulk density, water holding capacity and aggregate stability.

- Where highly acidic materials must be used as growing media, liming agents are generally applied to reduce acidity and metal solubility and to improve the availability of plant nutrients. Whilst short term pH buffering experiments may adequately predict the liming requirements of non-sulphide-bearing soils, they are of little use for sulphidic mine wastes as they do not take into account the long term Acid Generating Potential (AGP) of such materials.
- Currently there is no universally accepted method for estimating the AGP of mine wastes. Whilst hydrogen peroxide oxidation and acid-base accounting methods are widely employed in the coal mining industry (where pyrite is the main form of sulphide present) their utility for assessing the AGP of polysulphidic mine wastes containing appreciable quantities of non acid-generating sulphides is questionable.
- Although considerable research has been undertaken to investigate the affects of lime and organic matter addition to soils and innocuous mining wastes, there appears to have been relatively little research undertaken to investigate their use in amending very acidic, base-metal tailings (such as those present at the Tui mine site) for 'direct' revegetation purposes.

Chapter 4

Physical & Chemical Characterisation

4.0 Introduction

One of the primary objectives of this study was to identify the factors that have prevented the natural establishment of plants on the Tui Mine tailing for more than two decades. Although as discussed in Chapter 2 (section 2.4) several studies have focused on the impact of the Tui mining operation on surface and ground water quality very little research has been conducted to assess the chemical, physical and mineralogical properties of the tailings in relation to their potential use as a plant growth medium (Chapter 3, section 3.2.2.8).

This chapter reports the results of chemical and physical characterisation of the Tui tailings. A variety of parameters including; water-table variation, water infiltration, grain size distribution, penetration resistance, bulk density, pH, heavy metal, total sulphur and sulphate concentrations and acid generating potential (AGP) were assessed.

The Chapter is structured into 5 major sections; 4.1-*Preliminary Characterisation*, 4.2-*Physical Characterisation*, 4.3-*Chemical Characterisation*, 4.4-*Acid Generating Potential* and 4.5-*Chapter Conclusions*. The first of these sections (section 4.1) reports on chemical characterisation work that was initially conducted at the Tui mine site. The second section (section 4.2) describes the methodology and results of physical characterisation of the Tui tailings. Section 4.3 describes additional chemical characterisation that was carried to elucidate preliminary research findings presented in section 4.1. The penultimate section (section 4.4) focuses on the assessment of the tailings' Acid Generating Potential (AGP) and its variation with depth. Section 4.5 summarises results and draws conclusions as to characteristics and limitations of the tailings with respect to their potential use as a plant growth medium.

4.1 Preliminary Chemical Characterisation

To gain a fundamental understanding of the Tui Mine tailings' chemical characteristics in relation to their potential use as a plant growth medium, 3 sets of samples were collected from the tailings dam for analysis. The samples were taken at various depths (Table 4.1) from three pits excavated at sites S1, S2 and S3 that were positioned along a line running east to west in the central region of the dam (Figure 4.1). Samples of the cover material blanketing the western face of the dam were also collected for selected analysis (Plates 3.3 & 3.4). The cover material comprises angular pebbles and coarse to fine grained sands and is believed to have been a byproduct¹ originating from processing of the Tui ore.

Analyses conducted on the samples included; phosphate extractable sulphate, total sulphur, 6M HCl extractable Cu (copper), Pb (lead) and Zn (zinc) and pH in both water and hydrogen peroxide (H₂O₂). The results of these analyses are summarised in Tables 4.1 and 4.3. Multi-element analyses of two tailings samples obtained from site S2 was carried out using *inductively-coupled argon plasma atomic emission spectrometry* (ICP-AES). The results of these analyses are presented Table 4.2 and discussed in section 4.1.3.

4.1.1 Methodology

Prior to analysis the tailings samples were air-dried, sieved to less than 2mm and refrigerated at 4°C to minimise further oxidation of any sulphide minerals present in the tailings. Samples for metal and total sulphur analysis were ground to <150 µm before extraction or ashing.

4.1.1.1 pH (water)

The pH of the tailings was assessed using a standard method commonly used to assess the pH of mineral and organic soils (Blakemore *et al.*, 1987). The procedure involved the addition of 10.0g of air-dry tailings to 25.0 mL of distilled water. The samples were

¹ Many crushing plants used at the time when the Tui mine was operational were prone to losing specific grain-sized material (dross) during the ore crushing process. The material covering the dam batters is believed to have originated in such a manner and is thus likely to have contained appreciable sulphides.

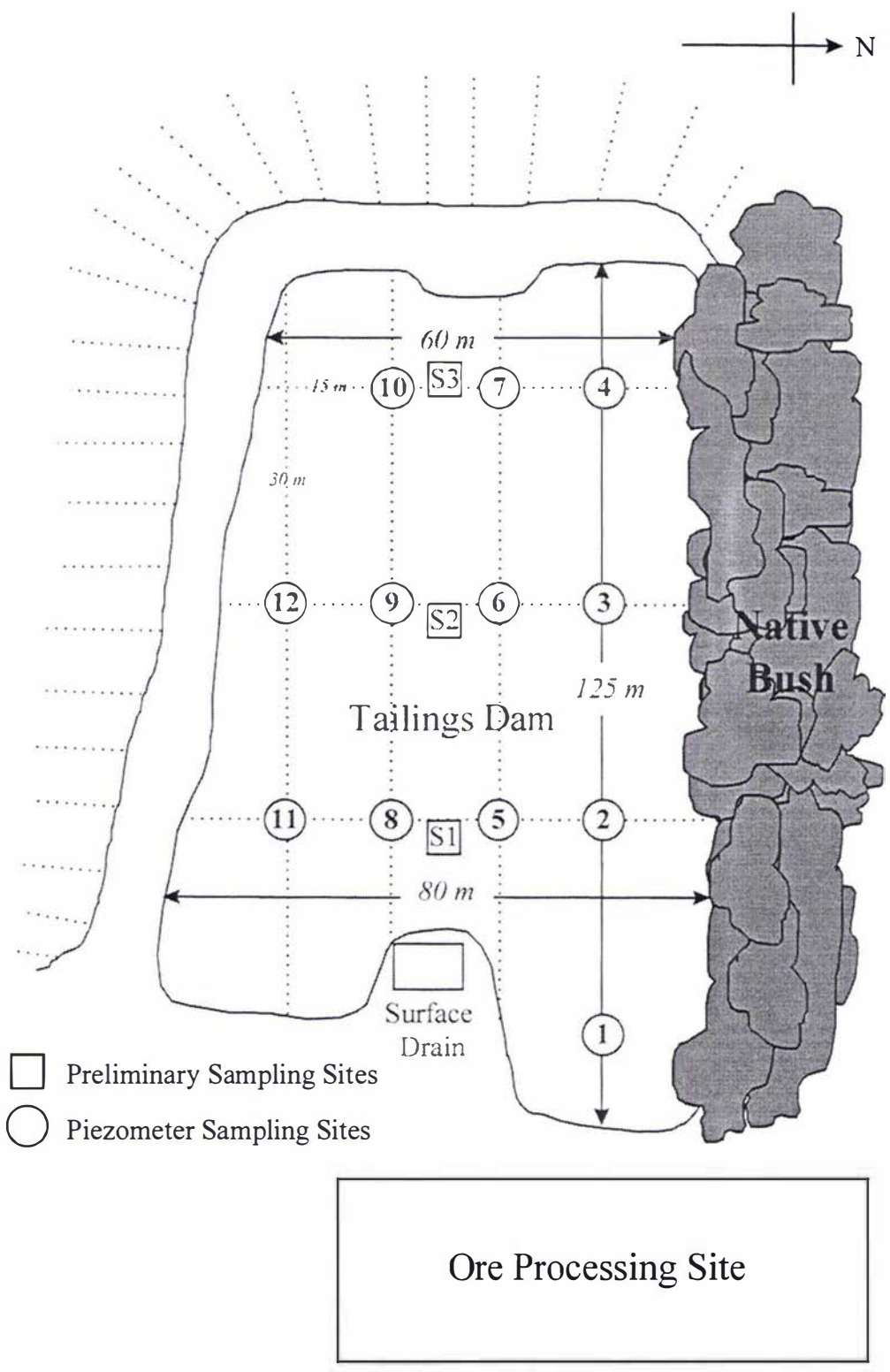


Figure 4.1 Schematic plan view of the Tui tailings dam indicating locations sites of the preliminary sampling and piezometer installation.
Grid sampling and piezometer sites coincide.

mixed in a 40-mL plastic beaker and left to stand for 12 hours. Prior to reading, the slurry was restirred and left to settle for 30 minutes. All pH analyses discussed in this study were conducted with a Radiometer PHM83 Autocal pH meter fitted with a Radiometer GK2401C combined glass/reference electrode.

4.1.1.2 pH (H₂O₂)

As mentioned in Chapter 3 (section 3.4.1.2) the oxidation reaction of pyrite and H₂O₂ is often used in the mining industry to screen sulphide-bearing overburden (Finkelman & Giffin, 1986). In an attempt to qualitatively assess the tailings' AGP, the pH of the samples was also measured after their reaction with H₂O₂. The method used in this study was based on that of Blakemore *et al.* (1987) and involved the addition of 25.0 mL of 30% analytical grade H₂O₂ to 1.0 g samples of tailings in 200-mL wide-mouth conical flasks. The samples were covered and reacted on a boiling water bath for approximately 30 minutes or until effervescence ceased. After cooling the samples were made up to original volume with distilled water, stirred and left to stand for 12 hours. Prior to pH measurement, the samples were again stirred and left to stand for 30 minutes.

An arbitrary pH value of ≤ 3.0 after H₂O₂ reaction was used to classify materials with the potential to generate substantial acidity (Blakemore *et al.*, 1987).

4.1.1.3 Total Sulphur

The concentrations of total sulphur (S) in the tailings samples were assessed using the sodium bicarbonate fusion method of Steinbergs *et al.* (1962). The method is outlined in Appendix 4(A) and essentially involved ashing a 0.25 g ground (<150 μ m) sample of tailings with 0.5g of sodium bicarbonate/silver oxide for 3 hours at 550 °C. The oxidised reactants were then solubilised with 5M hydrochloric (HCl) acid and diluted before total S concentrations were determined colourimetrically using an auto-analyser (Johnson & Nishita, 1952; Blakemore *et al.*, 1987).

4.1.1.4 Phosphate Extractable Sulphate

The phosphate extractable sulphate content of the tailings was assessed as per the method of Searle (1979). The method is fully outlined in Appendix 4(B) and is based on

the principle that phosphate ($\text{HPO}_4^{=}$) anions are generally sorbed more strongly to ‘soil’ particles than sulphate ($\text{SO}_4^{=}$) anions. The method essentially involved extracting the $\text{SO}_4^{=}$ from the tailings using a solution of 0.04M calcium hydrogen phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) at a tailings to extractant ratio of 1:5. The samples were shaken for 16 hours at room temperature (20°C), filtered and diluted as required. The $\text{SO}_4^{=}$ concentrations in the extract were again determined using an auto-analyser. Whilst it is recognised that some sulphide oxidation is likely to have occurred during the extraction procedure, the amount of $\text{SO}_4^{=}$ liberated is not postulated to have been significant over the limited time period involved (ie. 16 hours). Samples of a standardised soil² were included in all analytical runs of pH, $\text{SO}_4^{=}$ and total S to monitor instrument calibration.

4.1.1.5 Heavy Metal Concentrations

Concentrations of Cu, Pb and Zn in the tailings were determined using a GBC 904AA atomic absorption spectrophotometer using a recommended slit width of 0.5µm. Flame types, lamp currents and wavelengths used for these metals are reported in Table 4.9. The pseudo-total concentrations of metals were estimated by extraction with 6M HCl (analytical grade). The procedure involved the addition of 10 mL of 6M HCl to a 0.50g ground (<150 µm) sample of tailings (Brooks R.R, pers. comm.). The samples were heated for approximately ½ hour at 100°C on a hot plate before filtration with Whatman No. 41 and dilution to 100 mL with distilled water. Further dilution was conducted where necessary.

4.1.2 Results

4.1.2.1 Metal Concentrations

Initial characterisation of Tui Mine tailings indicated that some samples contain extremely elevated concentrations of Cu, Pb and Zn (Table 4.1). Pb concentrations in the tailings were particularly high with several of the samples found to contain in excess of 10,000 mg/kg. Cu and Zn concentrations in the tailings were comparable but generally much lower than those of Pb (Table 4.1).

² Manawatu Sandy Loam Standard #1 (Massey University, Department of Soil Science).

Although the concentrations of Cu and Zn were found to vary substantially within each profile, samples from corresponding depths were generally found to contain comparable metal concentrations. The Cu and Zn levels in the surface samples were relatively low and found to lie within the range for ‘normal’ soils (Table 4.2), however, the concentrations of these metals were found to increase substantially with depth (Figure 4.2). The trend in the distribution of Pb with depth, however, was not consistent at all the sampling sites (Figure 4.3a). The variable Pb content of the tailings is exemplified in the surface samples (0-50 mm), where Pb concentrations were found to range from 2498 to 11,761 mg/kg (Table 4.1).

Analysis of the coarse fraction (>2 mm) of the dam face cover material indicated that it contains comparable levels of Cu, Pb and Zn to the tailings (Table 4.1). This finding indicates that if the material originated from Tui ore as discussed in section 4.1, then despite its coarse grain size it has undergone extensive oxidation and leaching since its extraction and deposition.

Table 4.1 Selected properties of materials from the Tui mine site based on average values from duplicate analysis. See Appendix 4(C) for calculation of estimated sulphide percentages.
ND = metal concentrations were not determined.

Site	Depth [mm]	Total S [mg/kg]	SO ₄ ⁼ [mg/kg]	Sulphide S [%]	Cu [mg/kg]	Pb [mg/kg]	Zn [mg/kg]
S1	0-100	934	56	0.09	75	2498	112
	100-400	2130	245	0.19	147	4229	246
	400+	33977	1740	3.22	2015	12336	1831
S2	0-50	3483	36	0.35	269	11761	192
	50-150	1782	94	0.17	166	12503	193
	150-400	33171	483	3.27	644	10550	2880
	400+	40416	1185	3.92	3219	9502	2634
S3	0-100	2183	49	0.21	146	8852	430
	100-400	32469	670	3.18	451	12372	1319
	400+	41457	1200	4.03	1733	3227	2699
Bulk Sample	0-100	1624	20	0.16	ND	ND	ND
Dam Face							
Fine (<2mm)	0-100	4261	141	0.37	ND	ND	ND
Coarse (> 2mm)	0-100	3865	131	0.41	732	7010	1668

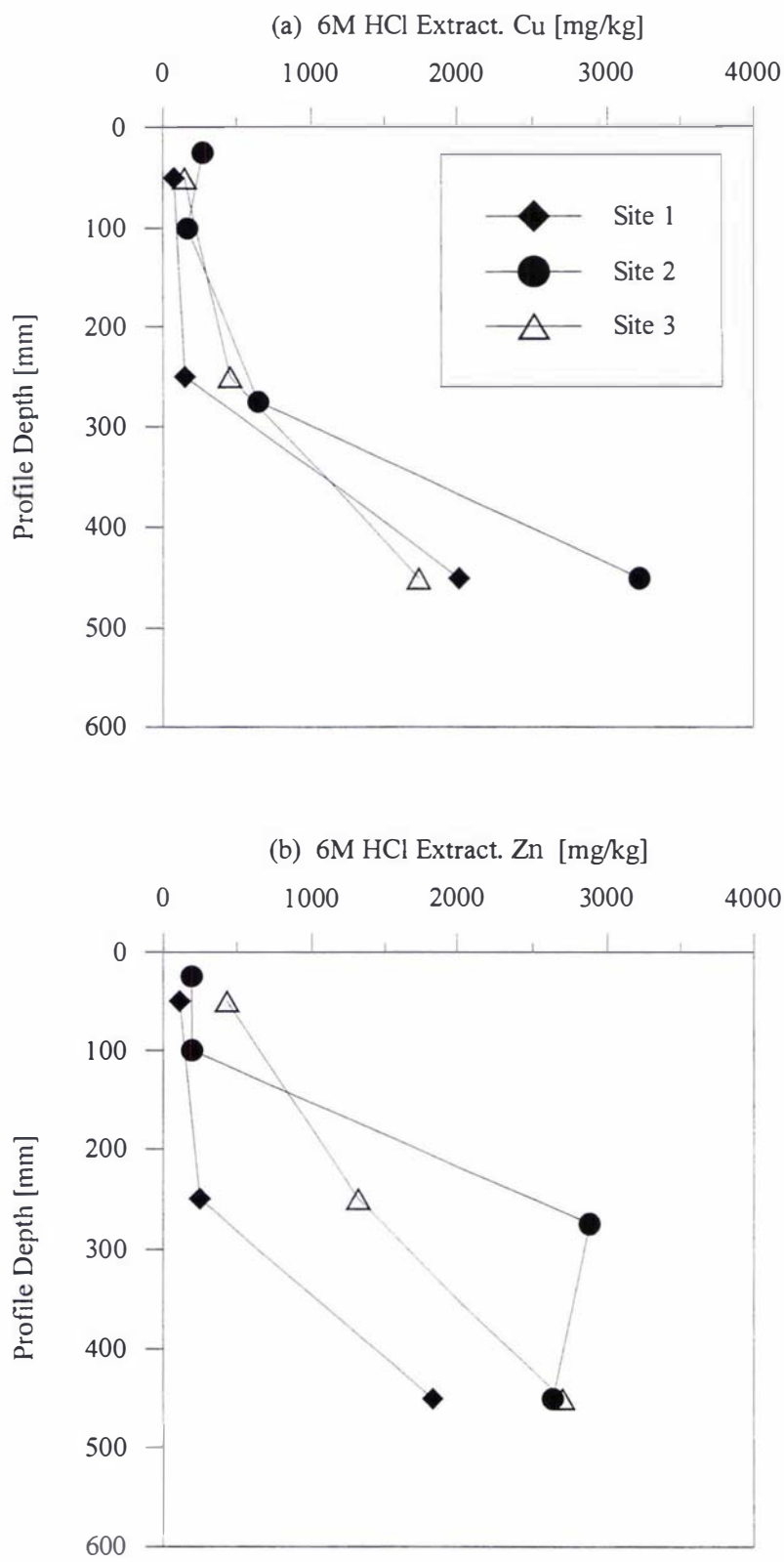


Figure 4.2 (a) 'Total' copper and (b) zinc versus depth at each of the 3 preliminary samplings sites

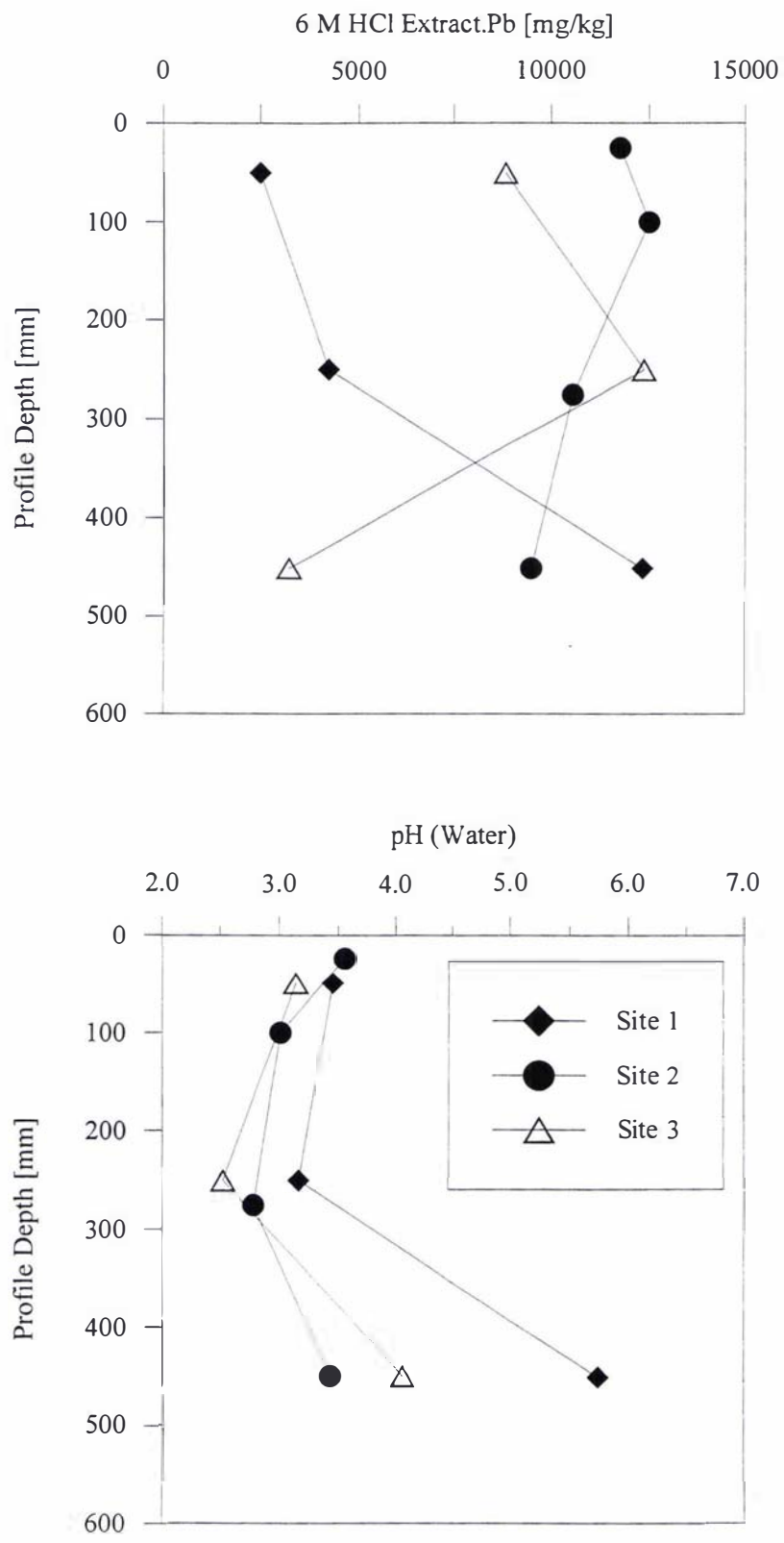


Figure 4.3 (a) 'Total' lead and (b) pH versus depth at each of the 3 preliminary sampling sites.

4.1.2.2 Total Sulphur & Sulphate Concentrations

Very high concentrations of total S and phosphate extractable $\text{SO}_4^{=}$ were also detected in some samples. In a trend similar to that exhibited by Cu and Zn, both total S and $\text{SO}_4^{=}$ sulphur were found to increase substantially with depth. Total S and $\text{SO}_4^{=}$ concentrations exceeding 33,000 and 1100 mg/kg respectively were detected in each of the 400+ mm samples. The concomitant increase of Cu, Zn and total S concentrations with depth indicated that these metals were present predominantly in the form of sulphides (Table 4.1).

Analysis of a bulk sample collected from the surface 100 mm of the tailings adjacent to site S3 indicated that the material contained similar $\text{SO}_4^{=}$ and total S concentrations to the surface sample at site S3 (Table 4.1). The concentrations of both total S and $\text{SO}_4^{=}$ sulphur were consistent with the concentrations of Cu, Pb and Zn in the tailings and indicated that the bulk sample contained relatively low concentrations of sulphide minerals (Table 4.1).

Sulphate and total S concentrations extracted from the cover material were comparable with levels found in the tailings and confirmed that both grain size fractions of the material contained relatively low concentrations of sulphide minerals (Table 4.1).

4.1.2.3 Plasma Emission Spectrometry

ICP-AES analyses were conducted on two samples obtained from preliminary sampling site S2 (Figure 4.1). The analyses were carried out by the New Zealand Pastoral Agriculture Research Institute on an Applied Research Laboratories 34000 simultaneous emission spectrometer. The total concentrations of 22 elements in the tailings were determined at two depths (0-50 mm and 400+ mm) to assess elemental variability with depth (Table 4.2).

With the exception of calcium (Ca), sodium (Na) and strontium (Sr), the concentrations of the measured elements were all found to increase with depth. Although elemental concentrations were generally far higher at lower depth, certain elements including As (arsenic), B (boron), Mo (molybdenum), Cu, Pb and Zn were present in the surface tailings at levels considered to adversely affect plant metabolism (Table 4.2). Of these

elements, As, B and Pb levels were particularly high and found to fall well outside the 'normal range' for soils (Table 4.2).

In contrast, total Al (aluminium) and Fe (iron) concentrations in the surface tailings were relatively low. Below 400 mm, however, the concentrations of Al and Fe increased to levels comparable with mean soil levels. Other elements that were found to exhibit substantial concentration increases with depth were As, Cd (cadmium), Cr (chromium), Cu, Se (selenium) and Zn. These elements were all present at concentrations well above the critical levels which delineate the potential onset of phytotoxicity (Table 4.2).

Table 4.2 Elemental concentrations of the Tui Mine tailings at preliminary sampling site S2 as determined by ICP-AES [mg/kg]. Bracketed data represent Cu, Pb and Zn levels determined by FAAS and S concentrations determined by sodium bicarbonate fusion. Sources: * = Bowen (1979); † = Kabata-Pendias & Pendias (1984) ♣ = Förstner (1995).

Element	Sampling Depth (0-50 mm)	Sampling Depth (400+ mm)	Median Level in Soils*	Normal Range in Soils*	Onset of Phytotoxic Levels†
Al	21334	49223		† 0.45-10 %	
As	252	1524	6.0	0.1- 40	15 - 50
B	2130	2396	10.0	0.9-1000*	25 - 100
Ca	164	87			
Cd	<1.8	26.5	0.35	0.01 - 2.0	3 - 8
Co	3.8	19.2	8.0	0.5 - 65	25 - 50
Cr	13.7	144	70	5 - 1500	75 - 100
Cu	149 (269)	4554 (3219)	30	2 - 250	60- 125
Fe	10 224	37 692	40000		
K	2466	3666			
Mg	361	439			
Mn	26.0	38.0	1000	2 - 10 000	1500 - 3000
Mo	16.9	45.0	1.2	0.1 - 40	2 - 10
Na	1536	1404			
Ni	<3.5	13.6	50	2 - 750	100
P	180	719			
Pb	2082 (11761)	2988 (9502)	35	2 - 300	100 - 400
S	3927 (3483)	42186 (40416)			
Se	<35.5	38.0		0.1 - 5	5 - 10
Sn	<3.8	5.1		1 - 200	50
Sr	14.8	7.4		2-600†	
Zn	204 (192)	3819 (2534)	90	1 - 900	70 - 400

Predictably ICP-AES sulphur concentrations in the tailings were high and comparable to the levels obtained using the sodium bicarbonate fusion method of Steinbergs *et al.* (1962). Cu and Zn concentrations determined by ICP-AES were similar to those determined by FAAS (Flame Atomic Absorption Spectrometry), whereas in the case of

Pb the former technique resulted in substantially lower values than the latter technique (Table 4.2). Subsequent FAAS and ICP-AES analysis confirmed that the Pb concentrations were very high in the surface tailings and that ICP-AES determined Pb concentrations in the preliminary samples were erroneously low. The reason for the disparity between the preliminary Pb results remains unclear but may have resulted from the formation of highly insoluble PbSO_4 during the ICP-AES extraction and dilution procedures.

4.1.2.4 pH (water)

The Tui tailings were found to be extremely acidic, particularly in the 50 to 400 mm sampling zone where pH values were typically between 2.5 and 3.0 and tended to be slightly lower than those found in the surface samples (Table 4.3). The pH of the tailings was found to increase below 400 mm indicating reduced hydrogen ion (H^+) activity. Similar pH profiles were obtained from each of the 3 sampling sites (Figure 4.3b).

Both grain size fractions of the dam face material were found to exhibit similar pH values in the vicinity of pH 4 and were thus slightly less acidic than the majority of the tailings samples (Table 4.3).

4.1.2.5 Acid Generating Potential

Upon treatment with 30% hydrogen peroxide (H_2O_2) the pH of all samples was found to fall to below pH 2.5 indicating the presence of appreciable quantities of acid generating sulphides (Table 4.3).

The pH data obtained from preliminary characterisation of the tailings was further used to estimate the relative reactivity of the Tui Mine tailings in terms of their Acid Generating Potential (AGP). Based on the known liberation of hydrogen ions (H^+) during sulphide and H_2O_2 reaction it was theorised that samples containing high concentrations of acid generating sulphides would liberate greater amounts of H^+ than samples containing relatively low concentrations. Using the pH of the samples after reaction with both water and 30% H_2O_2 , the change in hydrogen ion concentration (ΔH^+) was calculated as follows:

$$\Delta [H^+] = [H^+]_{H_2O_2} - [H^+]_{H_2O}$$

$$\text{Where } [H^+] = 10^{(-pH)}$$

The estimated concentrations of H^+ [mol/L] liberated during the oxidation reaction of each sample are presented in Table 4.3. Very approximate estimates of the Acid Generating Potential (AGP) of the tailings are also presented in Table 4.3 and were made by converting the ΔH^+ values for each sample into calcium carbonate equivalents in a similar fashion to the example presented in Appendix 6(B). The values presented in Table 4.3 were considered to be very crude because they were based on the assumption that changes to the sample to reactant ratio will affect the solution pH in a linear fashion. The relative magnitude of the values were, however, expected to be useful in identifying general AGP trends amongst the samples.

Estimates of the tailings AGP based on H^+ activity indicated that the AGP of the tailings was variable and apparently unrelated to depth (Table 4.3). This finding was contrary to what was expected as the trends demonstrated by Cu, Zn and total S were postulated to reflect an increase in the concentrations of acid generating sulphide minerals with depth. Higher concentrations of H^+ release and AGP values were therefore expected in the samples obtained from deeper within the profile.

To assess the validity of the AGP values obtained from H_2O_2 oxidation data, the AGP of the tailings was calculated stoichiometrically using the estimated sulphide S values as per the method outlined in Appendix 4(C). Although as discussed in Chapter 3 (section 3.4.1.1) estimates of AGP using sulphur data are widely employed in the coal mining industry, it was postulated that such a method would overestimate the AGP of the Tui tailings due to the presumed occurrence of relatively high concentrations of the non-acid generating sulphide minerals in the tailings³. The AGP (2) values presented in Table 4.3 were based on the assumption that all sulphide S in the tailings was present as pyrite (FeS_2).

³ Based on literature review outlined in Chapter 2 (section 2.6) galena (PbS) and sphalerite (ZnS) were predicted to be the primary non-ferrous sulphides present in the tailings.

Table 4.3 pH data and Acid Generating Potential (AGP) estimates [Mg CaCO₃/ 1000 Mg material] of the Tui dam materials based on (1) hydrogen ion liberation and (2) sulphur analysis.

Site	Depth [mm]	pH (H ₂ O)	pH (H ₂ O ₂)	$\Delta [H^+]$ [mol/L]	AGP (1)	AGP (2)
S1	0-100	3.45	1.62	2.36×10^{-2}	30	2.7
	100- 400	3.16	1.84	1.38×10^{-2}	18	5.9
	400+	5.74	2.06	8.71×10^{-3}	11	101
S2	0-50	3.55	1.59	2.54×10^{-2}	32	10.8
	50 - 150	3.01	1.97	9.74×10^{-3}	13	5.3
	150 - 400	2.78	1.81	1.38×10^{-2}	19	102
	400+	3.43	1.89	1.25×10^{-2}	16	123
S3	0-100	3.14	2.36	3.64×10^{-3}	5	6.7
	100 - 400	2.52	1.77	1.40×10^{-2}	20	99
	400+	4.06	2.04	9.03×10^{-3}	11	126
Bulk Sample	0-100	3.43	1.98	1.01×10^{-2}	13	5.0
Dam Face						
Fine (<2mm)	0-100	3.89	2.48	3.18×10^{-3}	4	12.9
Coarse (> 2mm)	0-100	4.07	2.27	5.29×10^{-3}	7	11.7

The AGP of the tailings, as predicted from sulphur/sulphate analysis, was found to increase substantially with depth at each of the 3 sites (Table 4.3). The AGP values of the 400+ mm samples were extremely high; at least 10 times higher than the surface samples at corresponding sites. Interpretation of the results presented in Table 4.3 indicate that for some samples liming rates in excess of 100 Mg of CaCO₃ would have been required to neutralise the acid theoretically produced by complete oxidation of 1000 Mg of tailings.

Regression analysis of values generated by the two AGP methods (ie. H⁺ generation versus sulphur) indicated that there was no significant interaction between the two parameters. The major reason for the disparity between the AGP estimates is believed to have resulted from the inability of the added volume of 30% H₂O₂ to fully oxidise sulphide minerals contained by some samples. Subsequent research was to show that substantially larger volumes of H₂O₂ were required to fully oxidise subsurface samples rich in sulphides (Chapter 4.3). Although this problem could have been readily

overcome by reducing the sample to H_2O_2 ratio no attempt was made to modify the procedure in the present study.

Another limitation identified with the assessment of AGP based on H_2O_2 oxidation was the variability of the pH values following reaction with the oxidant. The pH values obtained for the surface tailings at site S1 for example, were found to vary from 1.62 to 2.11 after H_2O_2 addition and reaction. When these values were used to estimate the AGP of the tailings, calcium carbonate equivalent values of 29.8 and 9.6 Mg CaCO_3 /1000 Mg of tailings were obtained respectively. The large disparity between duplicate samples highlights the crudity of this method to predict AGP values. Clearly, pH data generated by simple H_2O_2 methods such as that outlined section 4.1.1.2 must be used cautiously. It is evident that screening procedures should refrain from using pH measurements to rank the likely AGP of sulphide-bearing materials once identified.

It is postulated that the AGP estimates based on sulphur analysis better predicted the potential of the tailings to generate acidity. This hypothesis is substantiated by observed increases in 6M HCl extractable Cu and Zn concentrations with depth and by field observations which confirmed the presence of visible sulphide minerals within tailings originating from beneath 300-400 mm depth.

4.1.3 Conclusions on Preliminary Characterisation

Preliminary characterisation of the Tui Mine tailings indicated that the tailings are a hostile plant growth medium due primarily to their extremely acidic pH and elevated heavy metal concentrations.

Chemical analyses conducted on the various samples highlighted the extremely variable chemical nature of the tailings, particularly with depth. Samples obtained from corresponding depths at each site, however, were found to contain comparable concentrations of Cu, Zn, total S and $\text{SO}_4^{=}$ indicating that certain chemical parameters varied with depth in a predictable manner. Whilst total S, $\text{SO}_4^{=}$, Cu and Zn concentrations were lowest in the surface samples and increased substantially with depth, Pb concentrations in the surface samples were comparatively very high and well above the range normally found in soils.

Although the phyto-availability of Cu, Pb and Zn could not be estimated from the values obtained using the 6M HCl acid extraction procedure, it was postulated that the extremely acidic conditions prevailing in the upper tailings profile would render most labile metal forms readily available to plants. Strongly acidic conditions were found to persist throughout the profile but were particularly severe in the central region of the 3 profiles where pH values as low as 2.52 were encountered. Preliminary pH data indicates that this parameter is also depth dependent.

Hydrogen peroxide oxidation and elemental analysis indicated that the tailings contain appreciable quantities of acid generating sulphide minerals within 0.5 metres of the tailings surface. Correlation of these variables, however, was poor. Determination of the Cu, Zn and sulphide S concentrations indicated that the use of this H₂O₂ method to estimate the AGP of the tailings is inadvisable and that it should not be used to rank the relative reactivity of sulphide-bearing samples. Stoichiometric AGP estimates based on sulphur analysis were found to correlate well with Cu and Zn concentrations within the profile and are believed to far more accurately reflect the 'true' AGP of the Tui tailings.

Despite the disparity between the AGP results using the two different estimation approaches it is clear the tailings contained substantial amounts of reactive sulphide minerals and that more detailed chemical analysis was required to elucidate the tailings' AGP and the distribution and availability of heavy metals within the tailings dam. The lack of Fe concentration data with depth prevented better interpretation of AGP results.

Preliminary characterisation of the material covering the western and southern slopes of the dam (Plate 3.4) indicate that this material contains relatively low concentrations of sulphides minerals and has limited ability to produce acid. Based on this finding a decision was made to focus research on characterisation of the tailings as they were envisaged as being far more problematic to revegetate.

4.2 Physical Characterisation

4.2.0 Introduction

To facilitate further chemical characterisation of the Tui tailings, a series of twelve sampling sites (grid sites 1 to 12) was set up on the dam in a grid arrangement (Figure 4.1). At each of the 12 sampling sites a piezometer was installed. Although the primary purpose of the piezometers was to act as location markers for the sampling sites, they yielded valuable information relating to the position of the water-table within the Tui tailings impoundment. The water-table data collected from the 12 piezometers was compared with that obtained from four previously installed piezometers and is discussed below in combination with other physical characterisation work that was carried out during the course of this study.

4.2.1 Piezometer Installation

As a part of the monitoring program that has been conducted at the Tui Mine site, four piezometers have been periodically monitored by Works Consultancy of Hamilton over the past two decades. The piezometers are located at western end of the tailings embankment and it is believed they were installed during the dam's construction to monitor de-watering. Their installation, however, may have been prompted by a rainstorm in 1971 which seriously eroded the tailings. Subsequent storms during 1974 and 1976 also caused localised slumping of the dam and raised concerns regarding the stability of the dam (WRCM, 1991). Other factors that may have contributed to erosion of the tailings during these storm events include; the presence of artesian springs beneath the dam, the fine grain size of the tailings and the steepness of the surrounding terrain and tailings dam batters. It is the author's opinion that these factors, combined with the site's high rainfall, render the tailings long-term stability highly questionable despite the extensive stabilisation work that was carried out by the Catchment Board in 1976 (WRCM, 1991).

Water level data recorded from the 4 piezometers, which are now mostly dysfunctional, is held by the Matamata-Piako District Council. It indicates that the phreatic water-level in the tailings has generally rested more than 5 metres below the tailings' surface at the south-western corner of the dam. The water-table was found to rise towards the eastern end of the dam and intercept the surface of the tailings in the vicinity of site 11 (Figure

4.1). To obtain water-table data from elsewhere within the dam, 12 additional piezometers were installed in a grid arrangement that encompassed most of the dam’s surface.

The piezometers were constructed from 1.2 m lengths of 0.15 m internal diameter PVC drainage pipe. The bottom metre of the PVC lengths were drilled with a series of 10 mm diameter holes to enable ground water to flow freely into the tubes from the surrounding tailings. The perforated end of the piezometer tubes were inserted into pre-dug holes of approximately 1.0 m depth⁴ at each of the twelve sampling sites (Figure 4.1). After backfilling, removable plastic caps were fastened to the tops of the tubes and the piezometers were left to equilibrate for 24 hours prior to initial water level readings being taken.

4.2.1.1 Piezometer Results

The results obtained from the 12 piezometers were consistent with those obtained from the pre-existing piezometers and indicates that the water-table lies deeper than a metre below the tailings surface over much of the dam (Table 4.4). The 8 piezometers located at the western end of the dam were mostly dry at each inspection and are postulated to have remained largely devoid of water throughout the monitoring period. Although the exact depth of the water-table could not be determined due to the shallow installation depth of the piezometers, the absence of water within the top metre of the tailings profile indicates that a rising water-table is unlikely to adversely affect plant growth in the central and western regions of the tailings dam.

In contrast to these sites, the water-table at sites 1, 2, 5, 8, and 11 was usually found to lie within a half a metre of the tailings surface (Figure 4.1). On several occasions both during and after the monitoring period the water-table was observed either at or within a few centimetres of the tailings surface at these locations. The slight lowering of water levels in the piezometer tubes at sites 1, 2, 5, 8 and 11 during the summer months indicates that some seasonal variation may occur (Table 4.4).

⁴ This depth was considered adequate for the purposes of this study as it provided an insight into water-table effects within the potential plant rooting zone (ie. within the surface 1.0 m of the profile).

The piezometric data obtained during the monitoring period suggests that regardless of any seasonal variation, the water-table at and around these sites is likely to remain sufficiently close to the surface of the tailings to cause problems to establishing plants throughout the year. Permanent or extended periods of root zone saturation is a problem that any tailings reclamation scheme will have to address at the Tui mine site, particularly if it involves direct planting of the tailings.

Table 4.4 Piezometric data for the Tui tailings dam. Readings are in mm and refer to the distance of the water-table below ground level at the site. ‘Dry’ indicates that the water-tables lay below 1000 mm. Piezometers 1, 11 & 12 were not installed until the 30-11-92.

Date	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
10-11-92	-	20	Dry	Dry	180	Dry	Dry	250	Dry	Dry	-	-
13-11-92	-	140	Dry	Dry	100	Dry	Dry	150	Dry	Dry	-	-
30-11-92	250	0	400	Dry	0	Dry	Dry	30	Dry	Dry	100	Dry
15-02-93	450	350	Dry	Dry	460	Dry	Dry	280	Dry	Dry	350	Dry
07-03-93	400	300	Dry	Dry	400	Dry	Dry	150	Dry	Dry	300	Dry
18-06-93	230	100	Dry	Dry	100	Dry	Dry	40	Dry	Dry	140	Dry
03-12-93	Dry	340	Dry	Dry	600	Dry	Dry	800	Dry	Dry	530	Dry
26-08-94	70	40	Dry	Dry	30	Dry	Dry	50	Dry	Dry	40	Dry

Traditional drainage methods that use perforated pipes and/or gravel as a conduit for drainage water in subsoils are unlikely to lead to successful, long-term drainage of the Tui tailings. The potential inadequacy of such systems was highlighted by the piezometers installed at sites 2, 5, 8 and 11. These piezometers were found to continually refill with sediment upon cleaning due to the ingress of finely-ground tailings through the water access holes. Based on these observations it is therefore highly probable that sub-surface drains would quickly clog with tailings of low saturated hydraulic conductivity and cease to effectively drain the tailings.

The function of sub-surface drainage is likely to be further hindered by the distinctively layered nature of the Tui Mine tailings (Chapter 4.2.2). Due to observed textural variation between the layers it is probable that the coefficient of hydraulic conductivity in the horizontal direction is far greater than that in the vertical direction in many parts of the dam. In such circumstances exclusively vertical downward movement under

leaching can not be assumed (Easton-Groves *et al.*, 1982) and the efficacy of sub-surface drains is thus likely to be further diminished.

4.2.2 General Description

The distinctively layered nature of the Tui tailings is immediately obvious upon excavation of the tailings (Plate 4.1). The layers are readily distinguished by discrete changes in colour and/or texture and generally vary in thickness from a few mm to several cm. Although the colour of the individual layers vary considerably, two distinctive colour zones are evident in cross-sectional view (Plate 4.1). Chemical characterisation of the tailings will show that these two colour zones broadly relate to the oxidative state of the tailings and indicate a dramatic change in the AGP of the Tui tailings.



Plate 4.1 Tui mine tailings exposed in cross-section at grid sampling site 7.
This photograph highlights the layered nature of the tailings.

Smith & Sobek (1978) outlined the use of Munsell chroma values of powdered samples to evaluate the extent of oxidation in colliery spoils. They found a chroma value of 3 or more generally indicates that Fe oxidation has taken place and that there is probably an absence of pyrite. Chroma values of 2 or less were used to identify spoils in which Fe is absent or in a reduced state.

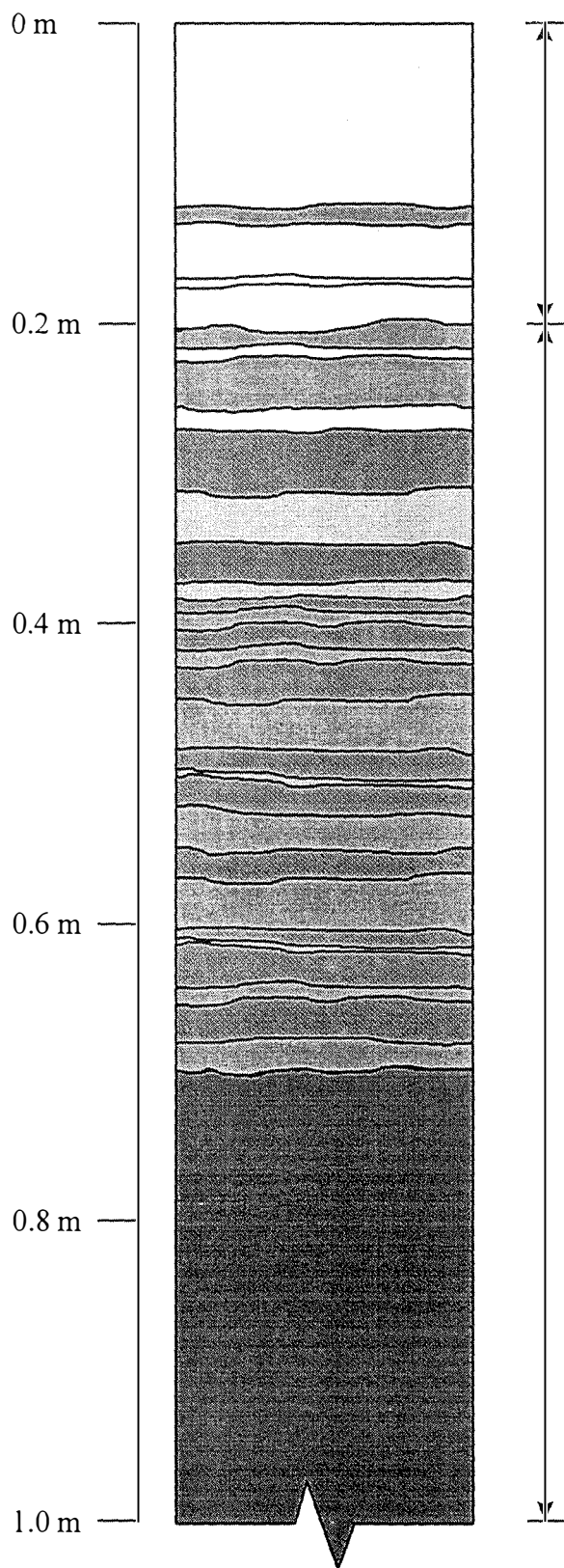
The laminae and layers of Tui tailings in the top 200 mm typically exhibit high chroma colours indicative of aerobic conditions (Figure 4.4). The tailings in this zone are characteristically *pale yellow* (2.5 Y 7/3)⁵ or *very pale brown* (10 YR 7/4). An abrupt colour change is generally observed at about 200 mm depth due to a presumed change in redox potential and the onset of predominantly anaerobic conditions deeper within the tailings' profile. The tailings below this depth are largely unoxidised and are characteristically *grey* (N 5/) or *dark grey* (N 4/) in colour.

The boundary between the two colour zones almost invariably occurs within 200 to 300 mm of the tailing's surface over most of the dam. The boundary is characterised by interlayered horizons of low and high chroma tailings that generally exhibit well-defined, non-gradational boundaries. The colour of the layers within this zone (200 to 300 mm) appears to be at least partially governed by grain size, with layers comprised finer-grained particles tending to exhibit grey colouring and coarser-grained layers, pale yellow and brown colours characteristic of the upper horizon.

Although most prevalent at the boundary of the two colour zones, isolated layers of grey (unoxidised) tailings were also found in the tailing's upper profile and at some locations exposed at the dam's surface. Much of the area bounded by sites 8, 9, 10 and 11 (Figure 4.1) for example, is covered by a 10 to 30 mm layer of fine-grained, dark-grey tailings. This layer was first noted during initial characterisation of the tailings in March 1993 and was still present in October of 1996. The fact that this layer of unoxidised tailings overlies about 300 mm of pale brown (oxidised) tailings and grey (unoxidised) tailings at depth indicates that some layers are relatively very resistant to oxidation and that air and moisture must be infusing laterally into the underlying tailings.

Shattered crusts of Fe-rich tailings were also found on the tailing's surface at several locations. These crusts are typically only a few to several millimetres in thickness and are generally dark brown in colour (*strong brown* 7.5 YR 4/6). XRD analysis of the crusts indicate they comprise primarily quartz, with minor kaolin, goethite and possibly some haematite.

⁵ Munsell Soil Colour Charts (USA)



Oxidised Zone - Tailings in the upper 0.2 to 0.3 m of the profile are typically *pale yellow* (2.5 Y 7/3) or *very pale brown* (10 YR 7/4) in colour, however, *pink* (5 YR 7/3), *white* (2.5 Y 8/1) and *pinkish white* (7.5 YR 8/2) are common colour variations exhibited by some layers. Isolated horizons of grey unoxidised tailings are often present in this zone. The surface tailings characteristically contain relatively low concentrations of sulphide minerals and most heavy metals, however, pH levels are generally extremely acidic.

Unoxidised Zone - Below about 0.2 m depth the tailings are largely unoxidised and are characterised by *grey* (N 5/) and *dark grey* (N 4/) colours. Layers in this zone often exhibit a bluish hue, particularly where the texture of the tailings is very fine. Tailings in this zone are characterised by relatively high concentrations of pyrite and associated sulphide minerals that are often visible to the naked eye. Heavy metal concentrations are accordingly high and pH conditions moderately acidic.

Figure 4.4 Cross-sectional diagram of the Tui mine tailings profile at grid sampling site 7

The majority of the Fe in the crusts is probably in the form of ferrihydrite, an amorphous Fe/Al compound not detected readily by XRD. It is postulated that these crusts formed as a result of the rapid oxidation of sulphide-rich tailings exposed at the tailings surface as the overlying, unconsolidated tailings particles were eroded by wind and water movement.

Several forms of hardpans are known to form in pyritic tailings including the reddish brown variety present at the Tui mine and a grey coloured variety that forms under reducing conditions from ferrous iron (Ahmed, 1995). Surface pans (such as those occurring at the Tui Mine) that form from the oxidation of pyrite-rich tailings are considered unstable as their electrochemical reactivity and structure render them susceptible to hydrolysis and dissolution in water (Ahmed, 1995).

4.2.2.1 Tailings Grain size

Despite obvious textural variation between individual layers, the grain size of the Tui tailings was relatively uniform, with the majority of particles falling in the range of fine sand (0.25- 0.1 mm) to silt (0.05-0.002 mm). The only site to show any marked variation in grain size was grid sampling site 1 (Figure 4.1) which was found to contain about 25 % angular pebbles (>4 mm) by weight in the surface 200 mm of the profile. The presence of this coarse material is attributable to the erosion and down-slope movement of crushed rock from the site of the old Tui ore processing plant (Plate 4.2).

A full-dispersion grain size determination was conducted on the six 100-mm incremental tailings samples⁶ to investigate the variation of grain size with depth (Table 4.5). The grain size fractionation method used was based on the wet pipette method described by Thomas (1973). As further discussed in Chapter 6 (section 6.4.2.1), the surface tailings (0-100 mm) at site 7 were found to contain a lower proportion of silt than most of the subsurface samples (Table 4.5). The relatively low concentrations of silt in the surface sample is believed to reflect post-depositional removal of the finer-grained tailings by wind and water erosion. Evidence of wind resorting is visible at the western end of the tailings dam adjacent to sites 4, 7 and 11 (Figure 4.1) where well-

⁶ The incremental samples were obtained from between 0 and 600 mm depth at grid sampling site 7 as discussed in section 4.3.1.2

sorted fine sand-sized tailings particles are found deposited on the inside edge of the wall of the tailings dam. These deposits are commonly greater than 300 mm thick and are protected from the prevailing westerly wind by the front wall of the dam.

Table 4.5 Particle size determination of site 7 incremental samples. Analyses are presented as a percent of oven-dry sample. Bracketed data = grain size range [mm] based on USDA classification.

Depth [mm]	Clay (<0.002)	Silt (0.002-0.05)	Very Fine Sand (0.05-0.1)	Fine Sand (0.1-0.25)	Medium Sand (0.25-0.50)	Coarse Sand (0.50-1.0)	Very Coarse Sand (1.0-2.0)
0-100	4.6	21.4	32.2	34.6	6.9	0.2	0.0
100-200	8.8	26.4	24.1	27.5	12.6	0.6	0.0
200-300	7.4	53.3	27.6	10.0	1.6	0.1	0.0
300-400	8.5	60.2	23.1	7.4	0.5	0.3	0.0
400-500	4.5	38.2	31.1	21.1	1.4	1.7	2.1
500-600	0.4	27.0	39.4	27.0	3.0	1.5	1.6

The oxidation and subsequent dissolution of fine-grained sulphide minerals in the surface tailings may have also contributed to the inferred depletion of silt-sized particles from the surface tailings. The high surface area of silt-sized particles renders them more susceptible to biochemical oxidation than coarser particles (Caruccio, 1975). Thus, any silt-sized sulphide minerals in the upper profile may have been preferentially oxidised and removed from the tailings by lateral or vertical drainage of the oxidation products in solution.

With the exception of the sample from the 500-600 mm depth, the clay fraction (<0.002 mm) of the tailings was found to be relatively uniform with depth, averaging about 6% (Table 4.5). XRD analysis of the tailings samples indicates that the clay in the samples is primarily kaolinite (Chapter 5) originating from the Tui ore (Courtney *et al.*, 1987).



Plate 4.2 Debris and degradation at the Tui mine site. The foundations of the Tui ore mill and processing site are visible in the top right hand corner of this photograph. Debris from this site including wood and angular pebbles were encountered at grid sampling site 1 (Figure 4.1).

4.2.2.2 General Discussion

The two distinctive colour zones observed in the Tui tailings are postulated to broadly equate with the *oxidation* and *reduction* zones described by Boorman & Watson (1976). During their investigation of abandoned base metal tailings they also identified a third zone, the *hardpan zone*. Ritcey (1989) cites several additional studies where similar mineralogical zones have been identified in materials ranging from uranium tailings to colliery spoil. These studies and the recent study by Lin (1997) indicates that tailings deposits often exhibit progressive change in mineralogical composition with depth to form distinctive zones. These zones develop with time and Ritcey (1989) likens the processes that form them to those that occur during pedogenesis and the weathering of mineral veins.

The *oxidation zone* (or *oxygenated zone* as it is referred to in the study of Garga *et al.*, 1983) is situated at the top of the profile where the tailings are exposed to atmospheric oxygen and moisture (Figure 4.4). Boorman & Watson (1976) found that base-metal tailings in this zone were characterised by depleted concentrations of Cu and Zn minerals and the presence of secondary anglesite (PbSO_4). They also identified that with the exception of Pb, the concentrations of metallic cations and sulphate present in the pore waters increased with depth.

Because the exchange of oxygen and the populations of aerobic bacteria are generally depth dependent the control of sulphide oxidation is considered by many as a surface problem (Sorensen *et al.*, 1980). The thickness of the oxidation zone is therefore governed to a large extent by the depth to which oxygen can ingress into the tailings. The low chroma colour of the Tui tailings indicates that diffusion of oxygen into the Tui tailings is largely confined to the upper 200 to 300 mm of the profile. The shallow oxidised zone is believed to reflect the Tui tailings' fine grain size which inhibits oxygen diffusion into the tailings.

The *hardpan zone* described by Boorman & Watson (1976) is often referred to as the *transitional zone* or *enrichment zone* and lies directly beneath the oxidation zone (Ritcey, 1989). Hardpans or *transitional zones* generally develop as a result of the precipitation of relatively insoluble compounds (eg. silica and metal oxides) from leachates percolating down the profile (Ritcey, 1989). The geochemistry of the transitional zone is therefore strongly influenced by the biogeochemical interactions and products of the overlying oxidised zone (Garga *et al.*, 1983). The deposition of alteration minerals in the transition zone may eventually fully impede drainage and root penetration (Lin, 1997). As the various reactions that take place during sulphide oxidation are quite dependent on the presence of oxygen and water the formation of a hardpan can potentially reduce the oxidation rate of tailings beneath the pan (Ahmed, 1995; Lin 1997).

The *reduction zone* of Boorman & Watson (1976) is sometimes referred to as the *redox* or *hypogene zone* (Garga *et al.*, 1983; Ritcey, 1989). This zone is analogous to the C horizon of a soil in that it represents the unweathered parent material of the tailings

profile (Figure 4.4). The mineral constituents of tailings within the reduction zone remain essentially unaltered. At the Tui mine site this zone is believed to prevail relatively near the tailings surface (generally within 300 mm of the surface) and is characterised by the onset of continuous and relatively uniform dark grey tailings.

4.2.3 Penetration Resistance

To investigate the presence of a sub-surface hardpan that could potentially inhibit plant growth by impeding root penetration and drainage, penetration resistance (PR) data was collected from sites 1 to 9.

Although hardpans occur naturally in pyritic (FeS_2) tailings they are more commonly associated with deposits rich in pyrrhotite (FeS) (Ahmed, 1995). The development and/or existence of a sub-surface hardpan in the *transitional zone* is dependent on a number of factors including; the mineralogical composition of the tailings deposit, the climate, the genre and abundance of bacteria, the disposal technique (eg. subaerial versus aerial tailings discharge) and the addition of liming agents (Ritcey, 1989). The occurrence and height of water-tables are also usually of critical importance to the formation of hardpans as they influence the precipitation and redissolution of reaction compounds within metalliferous tailings (Lin, 1997).

Although no distinct hardpans were detected during the excavation of sampling pits at grid sites 7 and 9, layers of more indurated tailings were encountered. The use of a cone penetrometer facilitated rapid quantification of the tailings PR at these sites and at other sites where high water-tables were known to persist throughout much of the year (section 4.2.1.1).

4.2.3.1 Penetration Resistance Methodology

Penetration resistance (PR) at the nine sites was measured with a Rimik CP10 Cone penetrometer to a depth of 450 mm. An in-built data-logger recorded penetration data at 15 mm intervals down the profile. Between 12 and 18 passes with the penetrometer were made within 2 metre radius of the piezometers at each site. The PR data obtained from the 9 sites was used to calculate an average PR value for each depth.

Tailings samples were taken from 3 zones (0-150 mm, 150-300 mm, 300-450 mm) to calculate the gravimetric water content of the tailings at each of the sampling sites. This enabled the effect of tailings' moisture content on PR to be assessed.

4.2.3.2 Penetration Resistance Results

The average penetration resistance (PR) of the tailings varied substantially, ranging from 605 kPa to 1545 kPa at sites 5 and 1 respectively (Table 4.6). The PR of the tailings also varied significantly with depth. Average resistance values at site 3, for example, ranged from approximately 450 kPa to nearly 3050 kPa (Figures 4.5b).

Although initially there appeared to be little similarity between the sites' penetration resistance profiles, closer examination of the plots indicated that most of the sites could be separated into two groups. Sites 1,2,5, and 8 all exhibited maximum resistance to penetration between 150 and 200 mm depth (Figure 4.5a), whereas the maximum penetration resistance at sites 3, 4, 7, and 9 was encountered between 350 to 400 mm depth (Figures 4.5b). Site 6 was the only site to exhibit no distinct profile maxima within either of these depth zones (Figure 4.6).

The fact that those sites exhibiting maximum PR deeper within the profile (ie. between 350 and 400 mm depth) were all found to lie in the drier central and western areas of the dam (ie. water-tables > 1.0 m deep) indicated that soil moisture content was possibly affecting penetration resistance. To further investigate the influence of the tailings' moisture content on cone penetration, penetration resistance data were averaged over 0-150 mm, 150-300 mm and 300-450 mm depths at each site and regressed against the gravimetric water content (ω) of the tailings assessed over the corresponding depths. Because 'soil' shear strength generally decreases with increasing 'soil' moisture content (McLaren & Cameron, 1990), the tailings' penetration resistance was predicted to negatively correlate with the gravimetric water content of the tailings

Six of the nine sites were found to show some correlation (ie. $r^2 > 0.5$) between water content and penetration resistances. Due to the low number of regression pairs, however, a significant relationship ($P < 0.05$) was only identified at one of the nine sites investigated (Table 4.6). Three of the sites (3, 4, 9) were found to exhibit a positive

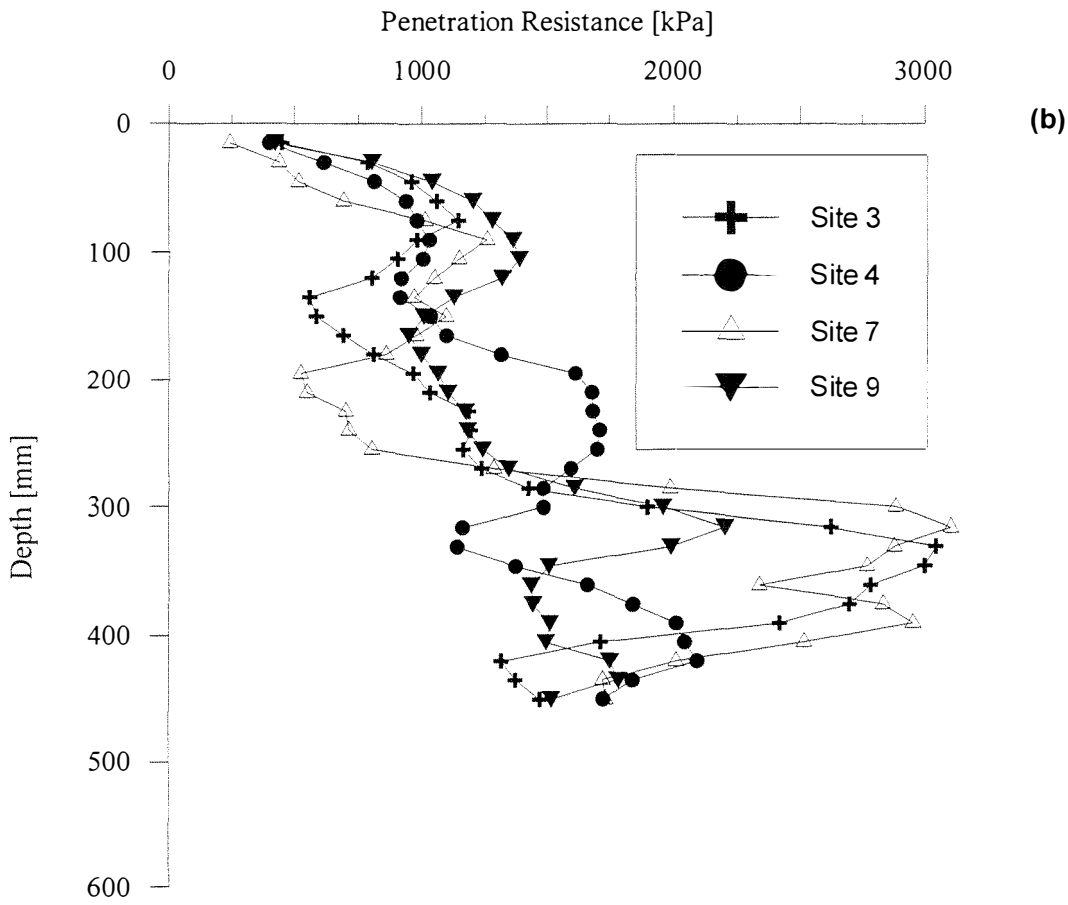
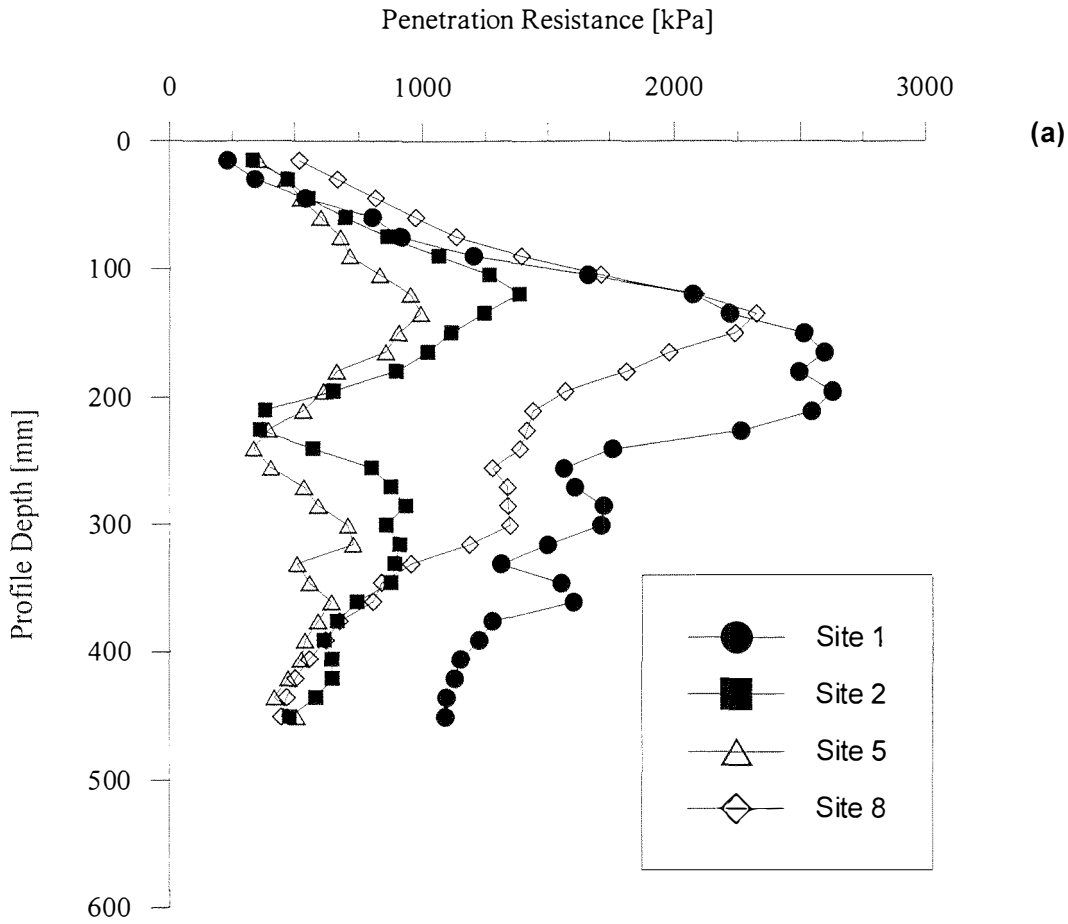


Figure 4.5 Tailings penetration resistance versus depth at specified grid sampling sites.

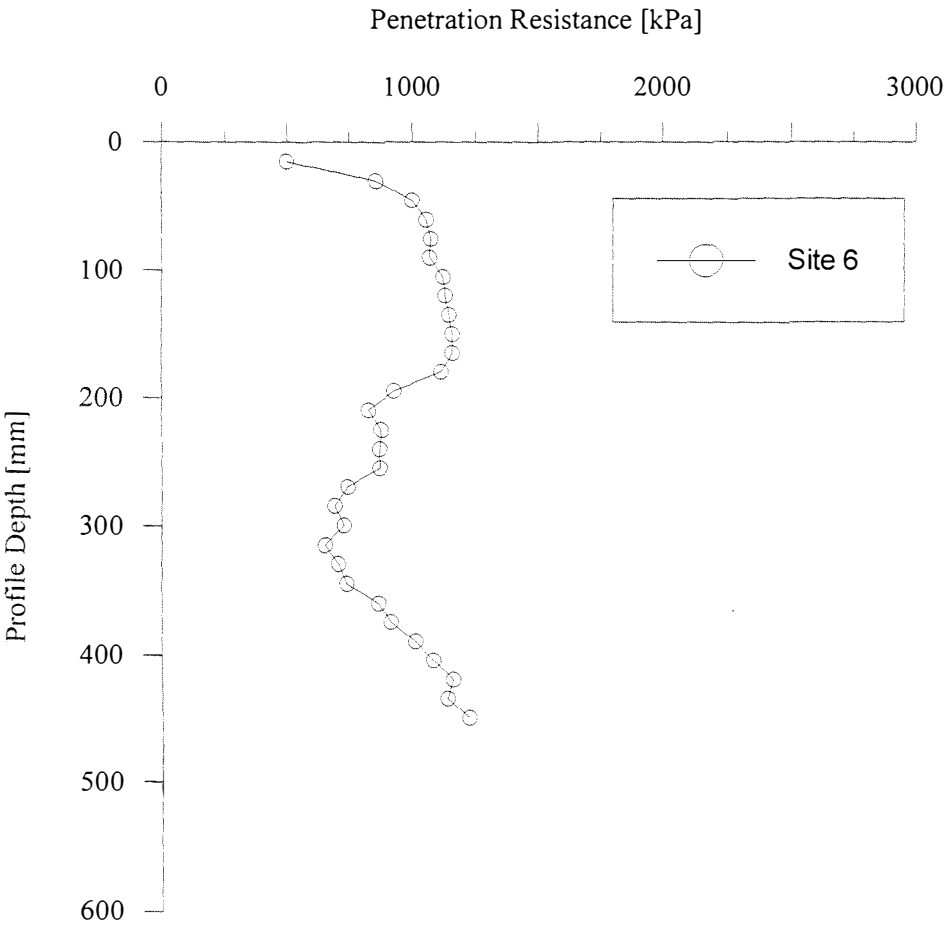


Figure 4.6 Tailings penetration resistance versus depth at grid sampling site 6.

relationship between PR and water content (ie. the PR of the tailings was found to increase with increasing water content). This finding contradicts predicted results in that high PR at these sites did not correspond with drier zones within the tailings’ profiles. Other factors such as bulk density, grain size and cementation were obviously collectively outweighing the effects of moisture content at these 3 sites which lay in the unsaturated central and western regions of the dam.

Table 4.6 Penetration Resistance (PR) data from Sites 1 to 9.

ω = gravimetric water content; S = significant (P<0.05); PS = possibly significant (P<0.1);
NS = not significant (P>0.1).

Sampling Site	PR Average [kPa]	PR Range [kPa]	PR Correlation with ω	r ² (significance)
1	1545	230 - 2628	-	0.05 (NS)
2	781	331 - 1386	Negative	0.984 (PS)
3	1410	451 - 3044	Positive	0.983 (PS)
4	1365	400 - 2093	Positive	0.968 (NS)
5	605	335 - 992	Negative	0.999 (S)
6	947	498 - 1222	-	0.01 (NS)
7	1341	424 - 2202	-	0.44 (NS)
8	1195	447 - 2323	Negative	0.64 (NS)
9	1487	241 - 3105	Positive	0.95 (PS)

Sites 2, 5 and 8, which demonstrated a negative correlation between PR and gravimetric water content, were situated at the eastern end of the dam where piezometric data indicates that the water-table remains close to the tailings’ surface throughout most of the year. The PR trends observed at these sites are postulated to simply reflect the relatively low water content of the tailings in the upper profile (Figure 4.5a).

The results of PR characterisation indicated that although no distinct subsurface hardpans have formed within the tailings, incipient cementation of the tailings may be occurring within specific horizons at some sites. At most sites, however, the average PR resistance of the tailings was below the widely recognised critical value of 2000 kPa⁷ indicating that plants roots should readily explore this medium should they establish.

⁷ PR values in excess of 2000 kPa are considered to restrict root penetration (Unger & Kaspar, 1994)

4.2.4 Infiltration Capacity

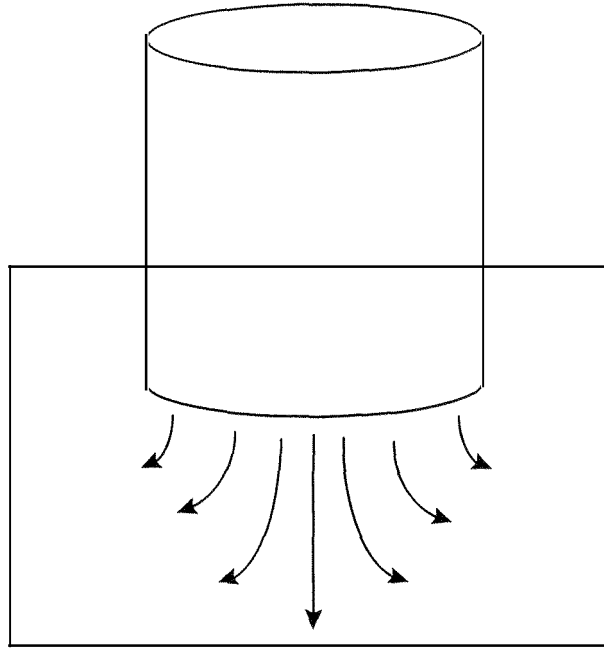
To assess the ability of the surface tailings to absorb rainfall, the infiltration capacity of the tailings was estimated in the field using ring infiltrometers. The infiltration capacity of the tailings was assessed at sites 7 and 9, where six ring infiltrometers were placed randomly within a 2 metre radius of each piezometer. Infiltration rates were measured over the first 5 minute period and then again after water had been continually ponded above the tailings for 30 minutes. The infiltration rates at both sites were found to have decreased markedly after this period and were believed to be at or very close to equilibrium.

The average infiltration capacity of the surface tailings at sites 7 and 9 were substantially different. Initial infiltration rates measured over the first 5 minutes were found to vary from 49 mm/hr at site 7 to as much as 1272 mm/hr at site 9. Although rates were found to vary at the individual sites, the surface tailings at site 7 generally had far greater capacity to absorb ponded water than the tailings in the vicinity of site 9 (Table 4.7).

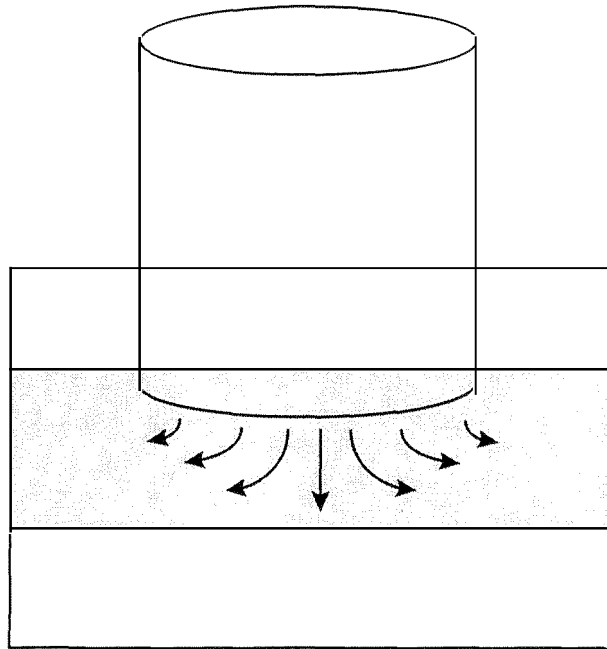
After the equilibration period the average infiltration rate at site 7 decreased dramatically, however, it was still relatively high (269 mm/hr) compared to site 9 where an average infiltration rate of less than 20 mm/hr was obtained (Table 4.7). Although intra-site variability was also significant the final infiltration rates at the two sites were again clearly different (Table 4.7).

Table 4.7 Average initial and final surface infiltration rates at grid sampling sites 7 and 9 based. The measurements were conducted in the field using ring infiltrometers. The standard deviation values presented are based on six replicate measurements made at each site.

Infiltration	Site 7 Initial Rate	Site 7 Final Rate	Site 9 Initial Rate	Site 9 Final Rate
[mm/hr]	773 ± 314	269 ± 50	35 ± 9	19 ± 8



Site 7 - The surface tailings at this site are predominantly fine-sand sized (0.25 and 0.1 mm) and exhibit relatively high infiltration rates (269 mm/hr).



Site 9 - The occurrence of a layer unoxidised tailings dominated by fine silt-sized particles substantially reduces the infiltration capacity of the tailings in the vicinity of site 9.

Figure 4.7 Schematic diagram explaining infiltration rate variability at grid sampling sites 7 and 9.

The substantial difference between the sites' infiltration capacities was explained upon removal of the infiltrometer rings from the tailings. It was found that the base of the infiltrometer rings at site 9 had penetrated either into or through a layer of extremely fine-grained tailings of low permeability (Figure 4.7). Although no more than a few cm in thickness, this layer was effectively controlling the infiltration rate of water into the tailings. Because no such layer was present in the surface tailings (0-100 mm) at site 7, the infiltration capacity of the tailings at this site was largely dictated by the rate at which the water could permeate through the comparatively coarse particles that generally dominate the surface 100-mm of the profile at most sites.

These results again demonstrate the variable nature of the tailings. As previously discussed (Chapter 4.2.2) certain areas of the dam (including site 9) have layers of finely ground tailings at or within a few centimetres of the dam's surface. The infiltration capacity of water at these sites is relatively low as evidenced by visible rilling and the formation of dendritic drainage patterns on the tailings following moderate to heavy rainfall events. Clearly the presence of low permeability layers near the dam's surface largely dictates the 'effective' rate of water infiltration at a given site.

4.2.5 Bulk Density

To assess the variability of the tailings bulk density with depth, 30 cores were taken from the field at grid sites 7 and 9 from 3 depths (Table 4.8). Samples were collected using aluminium cores of approximately 88 cm³ volume. The pre-weighed cores were driven vertically into the tailings at the 3 sampling depths with a wooden block and hammer. The samples were carefully removed by excavating around the core to prevent disintegration of the sample. After the cores had been trimmed and cleaned, the moist samples were weighed and dried in an oven at 105 °C oven for 48 hours. The samples were then reweighed to enable the dry bulk density of each sample to be calculated.

Results indicate that there is a slight increase in the bulk density of the tailings with depth at both sites (Table 4.8). In addition to greater compaction, this increase is believed to reflect the increasing abundance of higher density sulphide minerals with depth as discussed in section 4.4. Although there was some inter-site variation, the bulk density of Tui tailings at corresponding depths was comparable at sites 7 and 9. The

average bulk density of tailings at both sites were approximately 1.31 Mg/m³. This value although moderately high is comparable to many mineral soils (especially within subsoils horizons) and is therefore not considered likely to adversely effect plant root exploration.

Table 4.8 Average bulk density values [Mg/m³] of the Tui tailings at various depths. Values and sample standard deviations are based on 5 replicate cores.

Depth [mm]	Site 7	Site 9
0 - 50	1.30 ± 0.04	1.27 ± 0.02
200 - 250	1.32 ± 0.01	1.32 ± 0.02
400 - 450	1.33 ± 0.03	1.35 ± 0.05
Site Average	1.32 ± 0.03	1.31 ± 0.05

4.2.6 Conclusions on Physical Characterisation

Physically, it appears that the Tui Mine tailings pose no major limitations to plant growth. Characterisation conducted at the site indicates that the surface tailings have moderate bulk density and generally low to moderate resistance to penetration. Although layers of fine, uniformly textured tailings are believed to restrict oxygen diffusion into the tailings at some localities, the surface tailings (0-200 mm) generally appear to be sufficiently aerated to sustain plant growth. Two factors that may be inhibiting plant establishment, however, are the shallow water-table at the eastern end of the dam and the unconsolidated nature of the tailings.

The depth to the water-table was to found vary greatly about the dam. Piezometer results indicate that over most of the dam the water-table lies at least a metre below the tailings surface throughout much of the year. At sites 2, 5, 8 and 11, however, the water-table is believed to persist within 50 cm of the tailings’ surface during most months (Figure 4.1). The close proximity of the water-table to the tailings surface at these sites is of concern as it may lead to prolonged saturation of the plant root zone with potentially acidic and heavy-metal contaminated ground water. Problems arising from evaporative concentration of soluble salts during dry summer spells are envisaged to occur within areas proximal to sites 2, 5, 8 and 11 where evaporated pore-water may be quickly replenished via capillary action from shallow groundwater. To aid plant establishment in this region of the tailings dam, steps may have to be taken to either inhibit capillary rise or to substantially reduce the water-table height via open-channel drainage. The

thixotropic, fine-grained nature of the tailings may prohibit the use of 'traditional' subsurface drainage systems.

The unconsolidated nature of the tailings is likely to hinder attempts to revegetate the site by sand-blasting, upheaving and/or burying establishing seedlings. Methods to reduce wind velocity and hence the movement of abrasive particles across the surface of the tailings may be needed to improve seedling establishment. Water erosion will likewise pose a threat to establishing vegetation at the site.

The Tui tailings were generally found to exhibit penetration resistances of less than 2000 kPa within the potential root zone of the tailings (0-200 mm). This finding indicates that the roots of establishing vegetation should be able to adequately explore the root zone over most of the dam's surface. Although there is no clear evidence suggesting the presence of a distinct hardpan in the tailings profile, most sites exhibited indurated zones which generally occurred at one of two depths (150-200 mm or 350-400 mm). Because at several sites these zones coincided with those of maximum gravimetric water content the results indicate that some incipient cementation of the tailings may be occurring at specific depths.

4.3 Chemical Characterisation

4.3.0 Introduction

Based on the findings of the physical and preliminary chemical characterisation of the Tui Mine tailings (sections 4.1 and 4.2) it is evident that certain chemical properties are primarily responsible for inhibiting plant growth. No major physical limitations were identified, although as discussed in the previous section, the tailings do not provide an optimum growing medium in some areas of the dam due to poor aeration and drainage.

One of the primary findings of preliminary characterisation of the Tui mine tailings was that the tailings tended to vary considerably in their chemical composition. To elucidate the spatial variability of the tailings, further chemical characterisation was carried out at each of the 12 piezometer/grid sites. The variability of selected tailings' parameters with depth was also investigated at two of these sites.

4.3.1 Sampling Locations/Procedures

4.3.1.1 Grid Sampling at Sites 1 to 12

Composite tailings samples were collected from each of the 12 grid sampling sites at 0-100 mm and 100-200 mm depths for laboratory analyses. Characterisation concentrated mainly on the surface 200 mm of the tailings as it is this region of the profile that is generally most important in terms of seed germination and plant root growth. As discussed in section 4.1 and 4.2, the surface tailings were generally found to exhibit moderate to high chroma colours and relatively low 'total' concentrations of Cu, Fe and Zn, indicating that the tailings within this zone are aerobic and have probably undergone significant oxidation since their deposition.

The composite samples (each weighing about 1.0 kg) were made up of about 10 sub-samples collected within a 2 metre radius of each piezometer with a soil corer. The samples from each site were air-dried, passed through a 2 mm sieve and refrigerated at 4°C prior to thorough mixing and analysis.

4.3.1.2 Incremental Sampling

(i) 50-mm Incremental Samples

To study the variability of pH, phosphate extractable sulphate and total sulphur with depth, open pits approximately 1 metre deep were excavated at two randomly chosen sites (site 7 and 9). Sixteen 50-mm incremental samples were obtained from each site for analysis. pH analyses were conducted on an additional 6 samples at site 7 to a depth of 1200 mm.

At the time of incremental sampling four ‘bulk’ samples were also collected from two depths (0-150 mm and 150-300 mm) at each site. These samples each weighed approximately 1 kg and were collected and analysed to assess variability between the bulk and incremental samples.

(ii) 100-mm Incremental Samples

On a subsequent visit to the Tui mine site an additional six 100-mm incremental samples were collected at site 7 to a depth of 600 mm for the lime incubation trial reported in Chapter 6. To help interpret the results of the incubation trial the samples were characterised to assess the variability of the tailings’ Acid Generating Potential (AGP), chemical, physical and mineralogical properties with depth. The excavation pit from which these samples were obtained is shown in Plate 4.1.

4.3.2 Methodology

The pH of the tailings were determined in distilled water as per the method outlined in section 4.1.1.1. The total S and phosphate-extractable sulphate ($\text{SO}_4^{=}$) content of the tailings at sites 7 and 9 were again determined by the methods outlined in Appendices 4(A) and 4(B).

A literature review (Chapter 3.4.2) was undertaken to identify suitable extractants to characterise the tailings and to assess their AGP. The metal concentrations associated with the sulphidic and non-sulphidic fractions of the tailings were estimated from aliquots using Flame Atomic Absorption Spectrometry (FAAS) and are expressed in terms of the original air-dry mass.

Total and 'plant available' concentrations of selected metals were similarly assessed in the various tailings samples. With the exception of As (arsenic), metal concentrations in the extractants were determined using a GBC 904AA atomic absorption spectrophotometer. In the case of As, concentrations of this element were determined using a hydride generator. Arsine produced by the rapid addition of ca 5 mL of sodium borohydride solution⁸ to between 0.1 and 0.5 mL of sample solution was directly introduced to a GBC 909AA atomic absorption spectrophotometer via a heated silica tube (Robinson, 1994). The peak height of the absorption curve was used to measure As concentrations in the samples (Godden & Thomerson, 1980). The tube was heated to 950 °C using a GBC EHG3000 heating system to provide good atomisation of arsine.

With the exception of Al, As and Mn⁹ an oxidising air-acetylene flame was used to determine the various metals (Table 4.9). Recommended lamp currents, absorption wavelengths and a slit width of 0.5µm were used during the analyses (Athanasopoulos, undated). Where a wide range of metal concentrations were encountered more than one wavelength was often used to avoid excessive dilution of the samples.

The methodology of extraction procedures hence forth discussed in this section are fully reported in Appendices 4(D), 4(E), 4(F) and 4(G). Due to their very fine-grained nature (predominantly <250 µm), metal analysis of the tailings was generally carried out on the tailings after 2mm sieving unless otherwise stated.

⁸ The sodium borohydride solution contained 2% NaBH₄ and 1% KOH.

⁹ Al, Cd and Mn concentrations are discussed in Chapter 7.

Table 4.9 Flame type and lamp current settings generally used for atomic absorption spectrometry in the present study.

Metal	Flame Type	Flame	Lamp Current [mA]
Al	Nitrous oxide-acetylene	reducing	10.0
As	Flameless	-	3.0
Cd	Air-acetylene	oxidising	3.0
Cu	Air-acetylene	oxidising	3.0
Fe	Air-acetylene	oxidising	7.0
Pb	Air-acetylene	oxidising	5.0
Mn	Air-acetylene	stoichiometric	5.0
Zn	Air-acetylene	oxidising	5.0

4.3.3 Extractant Selection

One of the primary objectives considered during the selection of extractants that could be used to estimate the AGP of the Tui tailings was to identify extractants that would provide equally useful information relating to the ‘plant available’ and ‘total’ metal content of the tailings. In addition, the speed, simplicity and versatility of the extractants and/or extraction procedures was also considered.

The TAGP method outlined in section 4.4 required quantification of two forms of Cu and Fe in the tailings; acid generating (sulphidic) and non-acid generating (non-sulphidic) Cu and Fe. To estimate the ratios of non-sulphidic to sulphidic Cu and Fe, two extractants of different severity were thus required. A literature review undertaken to determine the extractants which were likely to fulfil the afore-mentioned requirements revealed that although a great deal of research has been undertaken investigating micronutrient extractants for soils, comparatively little research has been conducted looking at extractants suitable for estimating the plant-availability of ‘trace elements’ in metal-rich mining wastes (Chapter 3, section 3.4.2). Upon completing review of literature, however, it was decided to use and/or further evaluate the following three acid extractants; concentrated HF/HNO₃, 25% (v/v) HNO₃ and 0.1M HCl (Appendices 4(D), 4(E) and 4(F), respectively).

The 25% HNO₃ and HF extractants were compared to investigate the ability of 25% HNO₃ to assess the ‘total’ concentrations of Cu, Fe, Pb and Zn in the tailings. The two

extractants were predicted to release similar heavy metal concentrations because most heavy metals in the tailings were believed to be present in the form of sulphide minerals and thus not bound within silicate minerals (Chapter 3.4.2).

To elucidate the ability of hydrogen peroxide (H_2O_2) to oxidise and liberate sulphide-bound metals several samples were also reacted with this oxidant as per the method outlined in Appendix 4(G). After filtration the resulting supernatants were analysed for Cu, Fe, Pb and Zn.

4.3.3.1 Extractant Comparison

The materials upon which the various extractants were assessed included, surface (0-100 mm) and subsurface (500 - 600 mm) Tui mine tailings obtained from grid sampling site 7, two sulphide-bearing rock standards and a sample of pulverised pyrite. Three additional samples were prepared by combining the surface and subsurface tailings at 3 different ratios (7:3, 1:1, 1:3) to obtain samples containing approximately 20,000, 30,000 and 40,000 mg/kg of Fe respectively. The inclusion of these samples was designed to ensure that the data was normally distributed and to provide materials containing a range of metal concentrations comparable to those likely to be found within the upper metre of the tailings profile.

4.3.3.2 Validation of Analytical Results

The efficacy of the HF extraction and flame atomic absorption spectrometry (FAAS) procedures were validated by running CANMET¹⁰ (MP-1a) and CAAS¹¹ (Sulphide Ore-1) rock standards with the tailings samples. Due to the limited availability^{cf} of these standards, a 2 kg sample of Tui ore was ground to <150 μm and analysed by both ICP-AES and FAAS techniques for subsequent use as a standard. The certified standards proved to be useful reference material for the standardisation of the Tui Ore material and provided a means of optimising extraction procedures during the initial phases of the research program.

¹⁰ Reference data pertaining to this Zinc-Tin-Copper-Lead Ore standard can be obtained from the Canada Centre for Mineral and Energy Technology, 555 Booth Street, Ottawa, Canada.

¹¹ Analytical data for the CAAS standard is reported in Sine *et al.* (1969).

Analysis of HF/HNO₃ extracts showed levels similar to the standard values for Cu and Pb in the two standards (Table 4.10). Measured Zn concentrations in the CAAS standard were also found to agree well with the expected value, however, the procedure was found to overestimate the Zn content of the CANMET standard by about 12 %. This error is believed to have arisen during dilution of the supernatant which involved a 1000-fold serial dilution to bring Zn concentrations into the analytical range of the spectrometer.

Table 4.10 Comparison of average FAAS values with CANMET Ore standard MP-1a and CAAS Sulphide Ore-1 rock standard. VNR = values not reported

Metal	MP-1a			CAAS	
	Standard	HNO ₃	HF	Standard	HF
Cu	14400	11778	13345	8215	8621
Fe	VNR	56835	58292	VNR	279068
Pb	43300	43577	43607	249	233
Zn	190200	192637	213439	294	304

Although total Fe values were not reported for either of the standards, HF extraction results indicated that the CANMET and CAAS standards contained about 60,000 and 280,000 mg/kg of Fe respectively and that the 25% HNO₃ solution extracted about 97 % of the total Fe in the CANMET standard.

4.3.3.3 Assessment of 25% Nitric Acid Extractant

The Cu, Pb and Zn content of the MP-1a ore standard was also determined using the HNO₃ extraction procedure (Appendix 4(E)). This extractant was found to underestimate Cu levels in the standard, however, Pb and Zn concentrations compared well with recommended values (Table 4.10).

When the concentrations of 25% HNO₃ extractable Cu, Fe, Pb and Zn were regressed against the concentrations extracted by the HF method, a very highly significant ($P < 0.001$) relationship was identified in each case (Figures 4.8 & 4.9). The 25% HNO₃ solution was found to extract between 88% and 100% of the total metals in the tailings

as indicated by the regression coefficient values listed in Table 4.11. The coefficient values obtained in this study are consistent with those cited by Smith & Bradshaw (1979). In their paper they stated that the 25% HNO₃ extraction procedure extracts about 90 % of metals in sulphide-bearing mine wastes.

Table 4.11 Relationship between total (HF/HNO₃) metal concentrations versus 'pseudo total' (25% HNO₃). S** = P < 0.001

Statistical Variables	Copper	Iron	Lead	Zinc
Regression Coefficient (B value)	0.88	1.01	0.88	0.94
Coefficient of determination (r^2)	0.991	0.997	0.992	0.996
Significance	S**	S**	S**	S**

As shown in Figure 4.8b the 25% HNO₃ extractant was particularly efficient at extracting Fe from the tailings. This indicates that a negligible proportion of the total Fe is structurally bound with the silicate minerals constituting the tailings. Regression analysis results indicated that slightly lower percentages of Cu, Pb and Zn were extracted by nitric acid (Table 4.11).

4.3.3.4 Hydrogen Peroxide Oxidation

Results obtained from the oxidation of selected samples with excess 30% (analytical grade) H₂O₂ indicated that this method is unsuitable for estimating total metal concentrations in the tailings. The method was found to be time consuming and in the case of the sulphide rich samples involved the addition of large volumes (> 1.5 litres) of H₂O₂ to fully oxidise the samples. Due to the clear shortcomings of the method only four samples were subjected to hydrogen peroxide oxidation (Table 4.12). Where the measured values lie within the bounds of the regression graphs they have been plotted (Figures 4.8 and 4.9).

A linear curve was fitted to the Fe data and indicates that less than 10% of the total Fe in the samples was rendered soluble using this method (Figure 4.8b). The concentrations of Cu and Zn liberated into solution were generally found to be much greater than for Fe

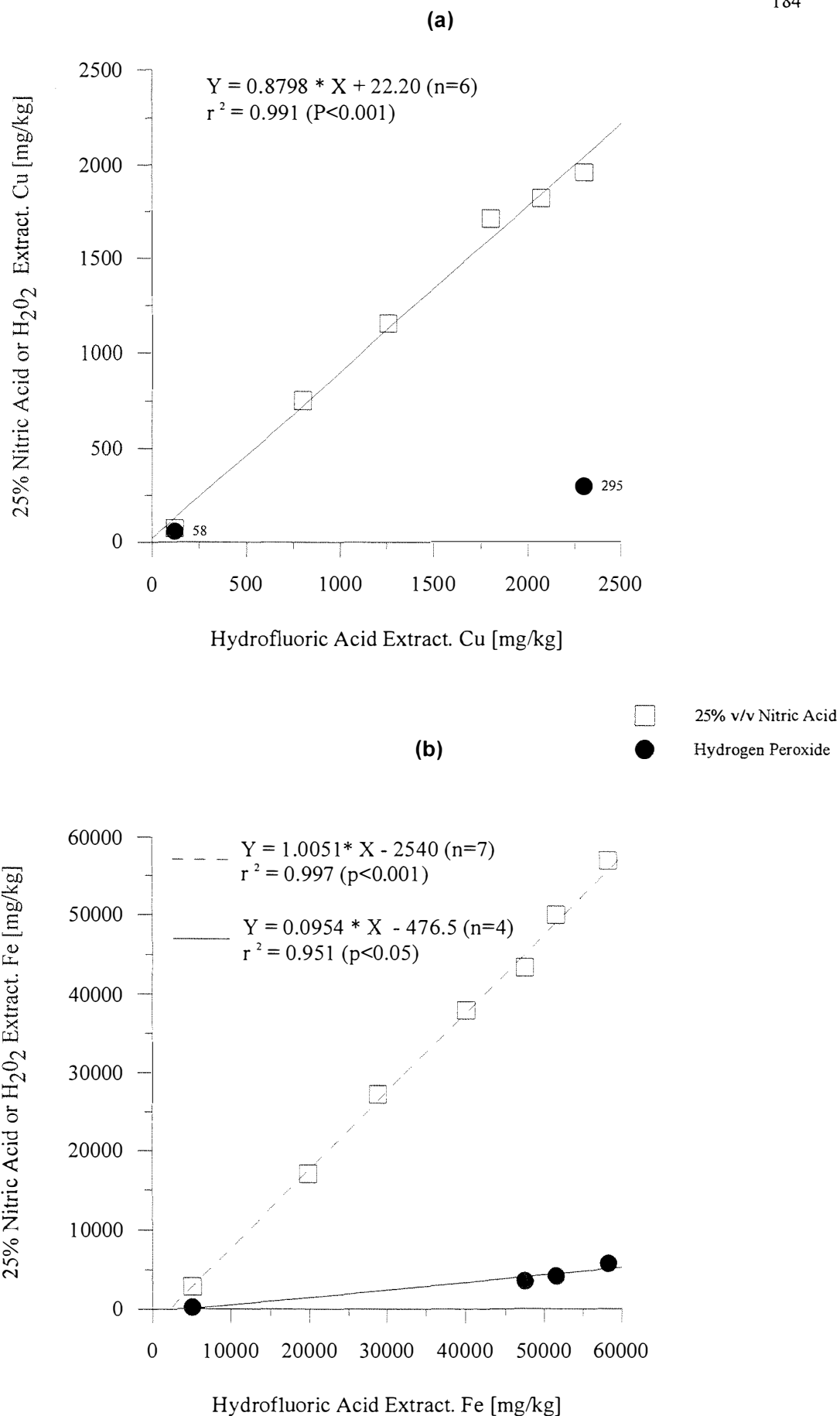


Figure 4.8 25% Nitric acid and hydrogen peroxide extractable (a) copper and (b) iron versus Hydrofluoric acid extractable concentrations.

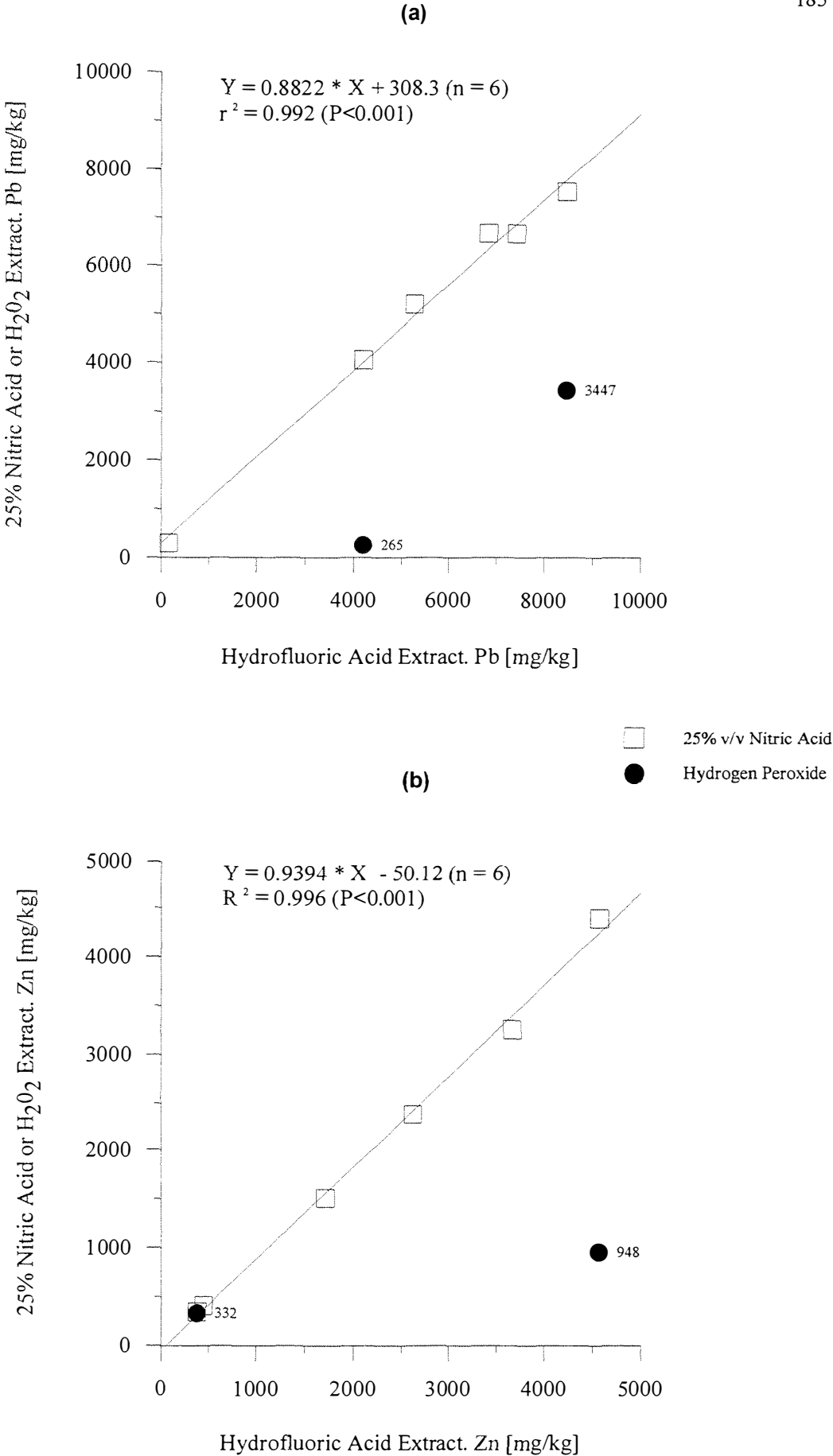


Figure 4.9 25% Nitric acid or hydrogen peroxide extractable (a) lead and (b) zinc versus Hydrofluoric acid extractable concentrations.

and Pb. For example, approximately 83% of the total Cu and 87% of the total Zn in the Tui Ore sample were solubilised using this method. Extraction ratios were lowest in the subsurface (500-600 mm) tailings sample from which 13 % Cu and about 21 % Zn was extracted (Table 4.12). The ratio of H₂O₂ ‘extractable’ Pb to total was variable ranging from less than 2% to over 40 % (Table 4.12).

These results reflect the variable solubility of sulphide oxidation products. It is postulated that Fe remains largely insoluble after hydrogen peroxide oxidation due to the formation of acid-stable, insoluble ferric-oxy-hydroxides. The formation of a red gelatinous precipitate during the oxidation of the samples substantiates this theory. Similarly, the probable formation of insoluble PbSO₄ (a primary oxidation product of galena) explains the generally low concentrations of soluble Pb in the oxidised samples. Unlike Fe and Pb, it is evident that Cu and Zn remained largely in solution presumably in the form of highly soluble metal sulphates.

Table 4.12 Percentage total Cu, Fe, Pb and Zn extracted by Hydrogen Peroxide procedure.

Sample	Cu %	Fe %	Pb %	Zn %
Mp-1a	77	9.9	7.6	74
Tui Ore	83	7.4	1.4	79
0-100 mm	48	3.0	41	87
500-600 mm	13	8.1	6.3	21

4.3.3.5 Discussion on Extractants

For the purposes of this study the 25% HNO₃ extraction procedure of Smith & Bradshaw (1979) proved to be a rapid and reliable means of quantifying the pseudo-total concentrations of Cu, Fe, Pb and Zn in the Tui Mine tailings. Measurements using standard geological samples indicated that HNO₃ achieved a good recovery of the total Cu, Pb and Zn. For the purposes of estimating ‘total’ metal contents in the tailings it was decided to use the 25% HNO₃ extraction procedure.

The use of H_2O_2 to oxidise the samples demonstrated the variable solubility of the various metal oxidation products. The ability of this method to liberate metals into solution was highly dependant on the nature of the sample (ie. tailings versus sulphide ore) and proved time-consuming. It was clear that in the case of Pb and Fe in particular, acidification of the sample with 0.1M HCl failed to solubilise the oxidation products formed during the oxidation of the various samples.

4.3.4 Metal Analysis of Incremental Samples

4.3.4.1 'Total' Extractable

The following subsection relates to characterisation of the six 100-mm incremental samples derived from site 7. The concentrations of 'total' (25% HNO_3) Cu, Fe and Zn were all seen to increase substantially with depth (Figures 4.10a & 4.11a). The relative order of abundance of these three metals in the tailings was identified as: $\text{Fe} \gg \text{Zn} > \text{Cu}$. 'Total' Fe concentrations were thus substantially higher than Cu and Zn concentrations and ranged from about 3,000 mg/kg in the uppermost sample to nearly 50,000 mg/kg in the 500-600 mm sample (Figure 4.10a).

Average Cu and Zn concentrations were both found to peak between 400 and 500 mm depth where levels exceeded 2100 and 5400 mg /kg respectively. Like Fe, the abundance of Cu and Zn were lowest in the surface 100 mm of the profile where respective concentrations of approximately 75 and 350 mg/kg were obtained (Figures 4.11a).

Similar to preliminary results reported in section 4.1.2, the distribution of Pb down the profile was found to contrast with that of Cu, Fe and Zn. Lead tended to be most abundant in the upper half of the profile and was the least variable of the major metals constituting the tailings (Figure 4.10a). Concentrations of Pb were found to peak at over 11,000 mg/kg between 200 and 300 mm depth. Although least abundant in the deepest sample (500-600 mm) Pb concentrations were still very high, exceeding 4000 mg/kg (Figure 4.10a).

4.3.4.2 0.1M HCl Extractable

The concentrations of 0.1M HCl extractable Cu, Fe, Pb and Zn in the 100-mm incremental samples were generally much less than the ‘total’ concentrations of these metals (Figures 4.10b and 4.11b). The amount of Fe, Pb and Zn extracted by 0.1M HCl was in most cases less than 10% of the total concentrations of these metals in the tailings (Table 4.13). In the case of Cu, however, the proportion of metal extracted by 0.1M HCl was generally far greater and increased markedly below 300 mm depth. The large proportion of Cu extracted by the relatively weak acid (0.1M HCl) indicates that beneath 300 mm depth more than half the Cu in the tailings is in a form that is potentially available to plants, presumably as relatively soluble Cu sulphates¹². The majority of Fe, Pb and Zn in the tailings, however, appears to be non-labile and is likely to be present in the form of largely insoluble sulphates, metal oxides and/or sulphides (Table 4.13). Whilst total As levels were not assessed in the HNO₃ extractants, 0.1M HCl extractable As was determined and found to be present in similar concentrations to Fe (Figure 4.10b).

Table 4.13 Percentage of total metal extracted by 0.1M HCl in site 7 incremental samples and grid samples. NA = not analysed

Depth [mm]	Cu %	Fe %	Pb %	Zn %
Site 7				
0 - 100	32	6	14	9
100 - 200	23	5	8	15
200 - 300	10	1	5	3
300 - 400	75	3	4	13
400 - 500	52	6	4	4
500 - 600	69	3	6	5
Grid Samples				
0-100 (range)	12.8 (4.3 -28.9)	2.8 (1.45 - 5.2)	NA	NA
100-200 (range)	19.1 (7.2 - 31.7)	6.1 (1.7 - 35.1)	NA	NA

The distribution of 0.1M extractable Cu, Fe Pb and Zn within the profile were similar to that of the total concentrations (Figures 4.10 & 4.11). In contrast to Cu, Fe and Zn

¹² The absence of organic matter and specifically humus which is responsible for strongly complexing Cu in soils (Alloway, 1995) undoubtedly increased the availability of this metal in the tailings.

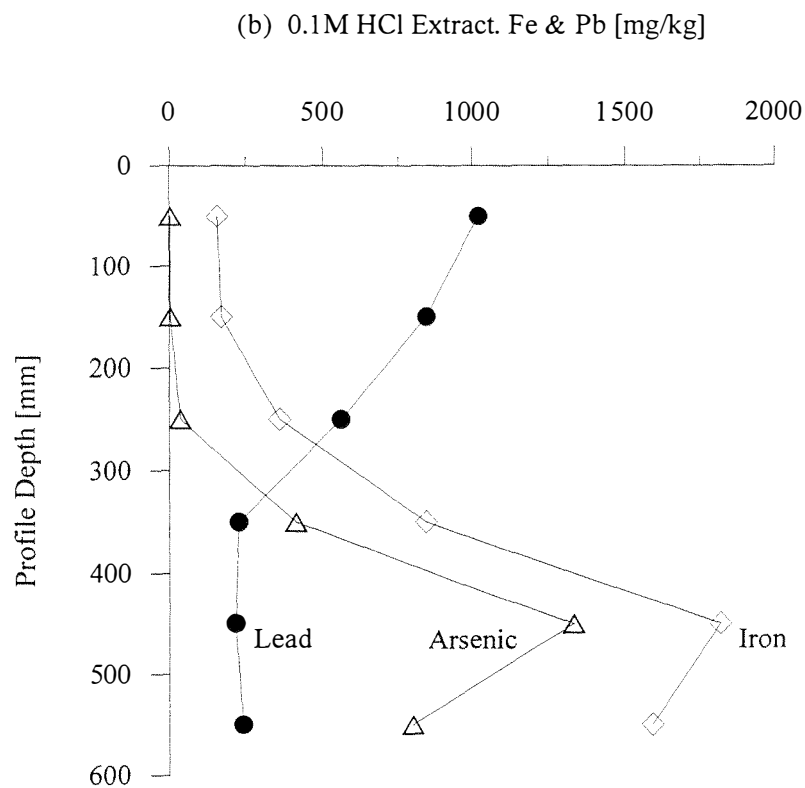
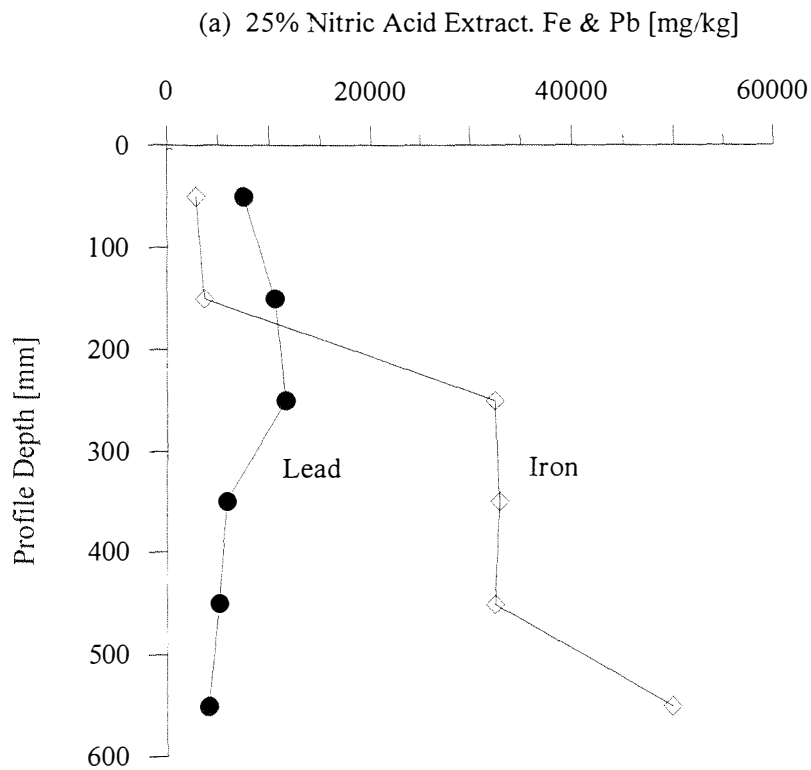


Figure 4.10 (a) 25% Nitric acid extractable Fe and Pb and (b) 0.1M HCl extractable As, Fe and Pb versus depth.

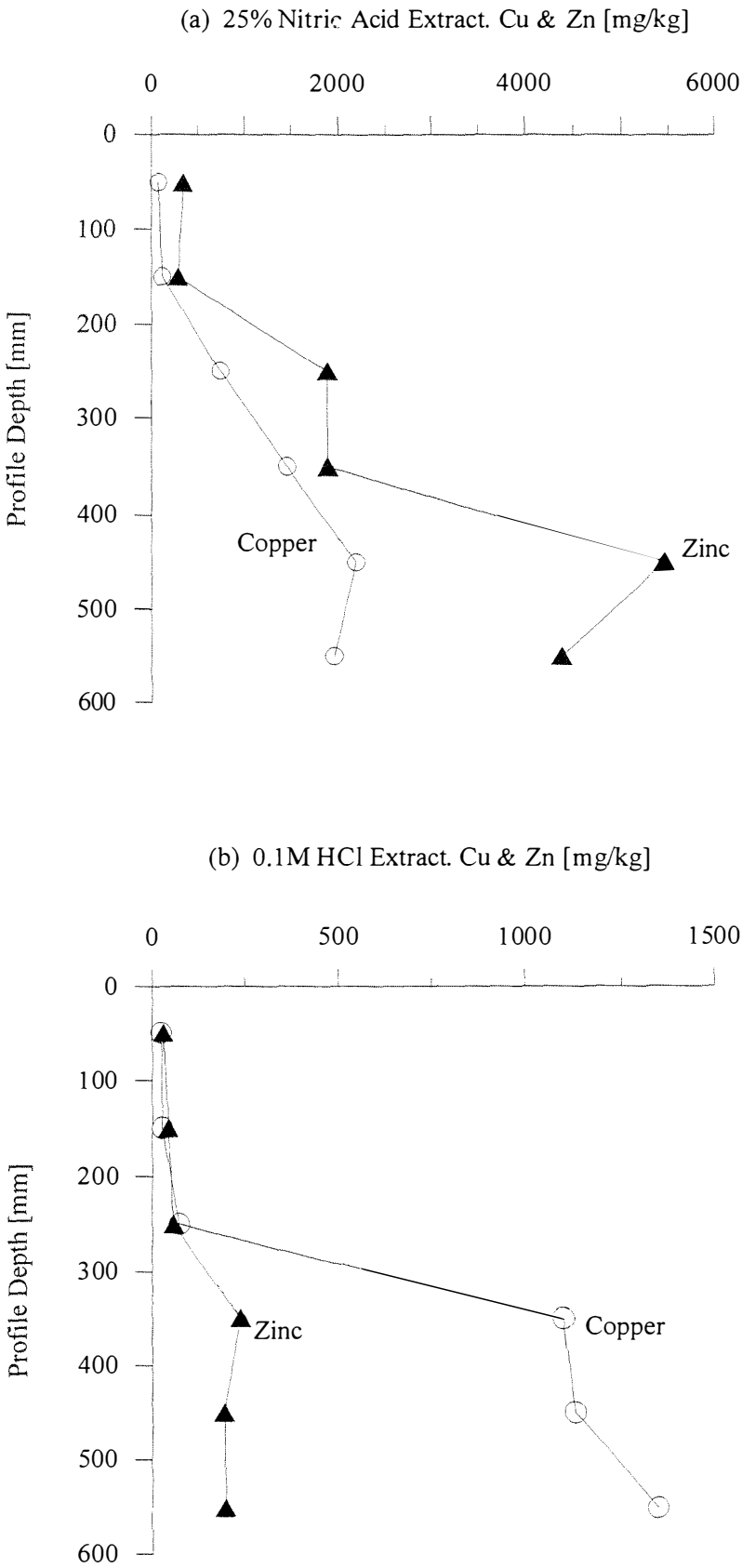


Figure 4.11 (a) 25% Nitric acid extractable Cu and Zn and (b) 0.1M HCl extractable Cu and Zn versus depth.

concentrations, 0.1M HCl extractable Pb concentrations were greatest in the top of the profile where XRD analysis indicated that the majority of Pb was present as highly insoluble anglesite (PbSO_4) (Chapter 5). Despite the high concentrations of PbSO_4 in the surface tailings, 0.1M HCl was found to extract relatively little of the ‘total’ Pb in the tailings, indicating that this extractant only partially solubilises anglesite (Table 4.11). This result is consistent with findings from the H_2O_2 oxidation extraction procedure (Chapter 4.3.3.4) and Eh-pH data which indicates PbSO_4 is stable at pH levels induced by 0.1M HCl (ie. $\text{pH} \approx 1.0$) (Brookins, 1988).

Regression analyses of the Cu fractions identified a highly significant ($P < 0.01$) positive correlation between 0.1M HCl and ‘total’ Cu concentrations in the incremental samples (Figure 4.12a). Iron and Zn were also shown to exhibit significant ($P < 0.05$) relationships between 0.1M HCl extractable and ‘total’ metal concentrations provided the data were logarithmically transformed where necessary prior to regression analysis (Figure 4.12a & 4.13b). Although logarithmic transformation of the log-normally distributed Pb data improved correlation between the two sets of data the relationship was weak ($P < 0.1$) and only possibly significant (Figure 4.13a). Circled surface samples (0-300 mm) in Figures 4.13a & 4.13b, demonstrate the contrasting trends with depth and metal concentration between Pb and Zn.

Although the positive (and generally significant) correlation between the 0.1M HCl and total metal concentrations in the incremental samples indicates that the amount of readily soluble (non-sulphide) metal compounds is increasing with depth in a similar proportion to total metal concentrations, it is possible that the dilute acid extractant is capable of dissolving small proportions of the sulphide-bound metals and therefore the concentrations of non-sulphide metals are not in fact increasing.

Analytical results obtained from characterisation of the surface (0-100 mm) and subsurface (100-200mm) grid samples indicate that in the case of Fe the positive correlation (between Fe fractions) is related to the depth distribution of more soluble forms of non-sulphide Fe (section 4.3.5). In the case of Cu, however, a significant relationship between total and 0.1M HCl extractable concentrations was identified not only in the incremental samples obtained from site 7, but also in the surface and

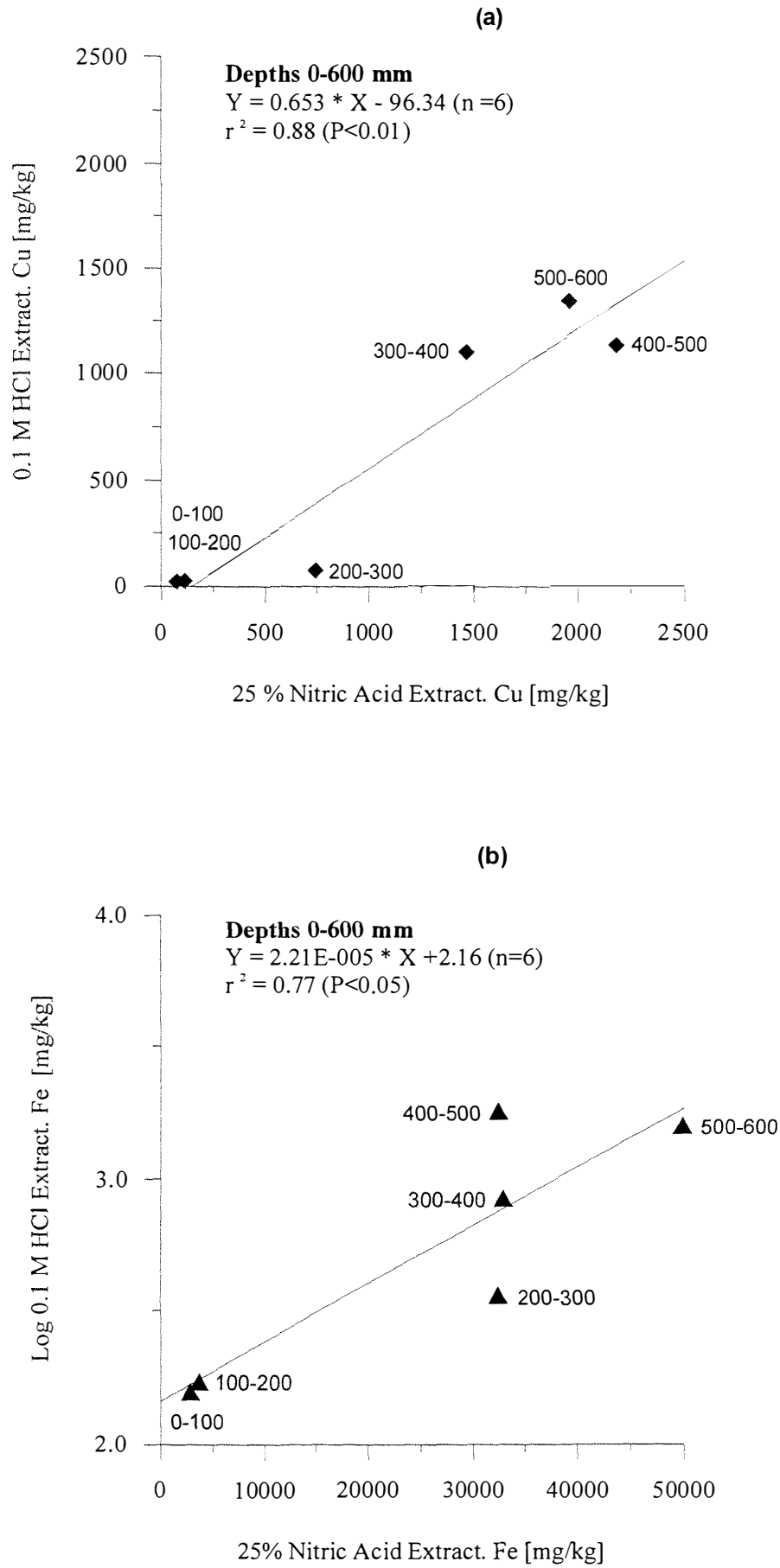


Figure 4.12 (a) 0.1M HCl Cu versus 'Total' Cu (b) Log 0.1M HCl Fe versus 'Total' Fe.

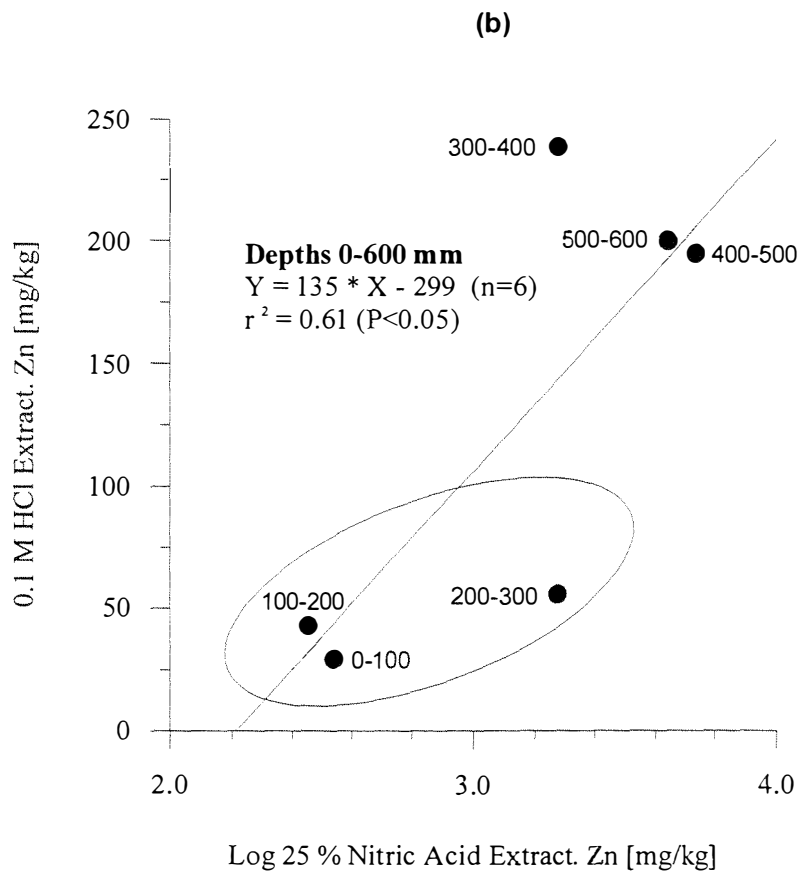
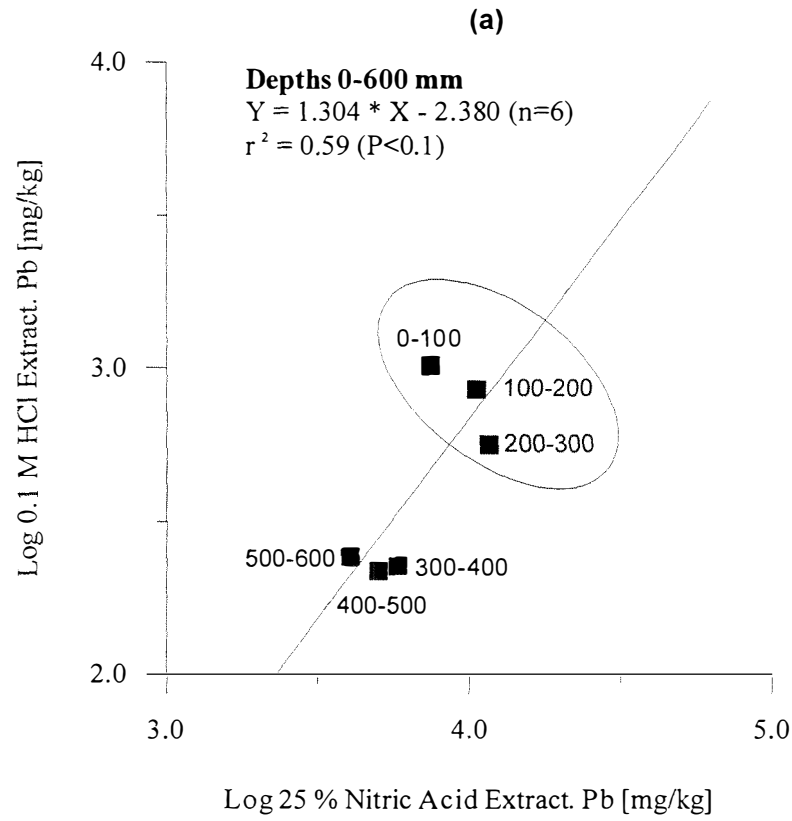


Figure 4.13 (a) Log 0.1M HCl Pb versus Log 'Total' Pb and (b) 0.1 M HCl Zn versus Log 'Total' Zn.

subsurface grid samples (section 4.3.5). Although this finding indicates that 0.1M HCl may be solubilising sulphide-bound Cu, the fact that the 0.1M HCl to ‘total’ Cu ratio changes considerably from sample to sample suggests that the mineralogical form of the Cu has an important bearing on the amount Cu being extracted by 0.1M HCl.

4.3.5 Metal Analysis of Grid Samples

4.3.5.1 ‘Total’ Extractable

The metals of primary interest at the grid sites were Fe and Cu as they are associated with acid generating sulphide minerals chalcopyrite (CuFeS_2) and pyrite (FeS_2). Although the oxidation of Zn and Pb bearing sulphide minerals is not believed to liberate significant quantities of acid, the concentrations of these metals was also determined at sites 1 to 12 (Table 4.14). Interest in these metals stemmed from preliminary characterisation of the tailings (section 4.1.2) which indicated that Pb and Zn were present in the tailings in potentially phytotoxic concentrations.

Table 4.14 Average and range of Cu, Fe, Pb and Zn [mg/kg] in grid samples extracted by 0.1M HCl and/or 25% v/v HNO_3 . Log-normally distributed metal concentrations are presented with standard deviation ranges.

Metal	Extractant	Average	STD Range	Site Range
0-100 mm				
Cu	0.1M HCl	6	3 - 12	2 - 40
	HNO_3	68	39 - 117	26 - 148
Fe	0.1M HCl	149 ± 73		56 - 345
	HNO_3	5239	4137 - 6635	3642 - 8762
Pb	HNO_3	11934 ± 6997		2522 - 27416
Zn	HNO_3	255	149 - 438	123 - 973
100-200 mm				
Cu	HCl	19	5-76	3 - 314
	HNO_3	135	48 - 375	28 - 991
Fe	HCl	261	140 - 486	96 - 773
	HNO_3	6805	2976 - 15559	1503 - 22387
Pb	HNO_3	12392 ± 7009		2016 - 22263
Zn	HNO_3	512	206 - 1273	162 - 2333

Metal data, as determined by FAAS, indicate that the concentrations of Cu, Fe, Pb and Zn vary substantially from site to site within the tailings dam (Table 4.14). Without exception the subsurface tailings (100-200 mm) were found to contain greater ‘total’

metals than the surface tailings (0-100 mm). To assess whether the variance in metal content and mean metal concentrations were significantly different between the surface and subsurface samples the data were interpreted using two commonly used statistical tests; the **F**-test and the standard **t**-test (Brooks, 1983).

The **F**-test was used to compare the population variances of the surface (0-100 mm) and subsurface (100-200 mm) metal data¹³. In the cases of ‘total’ Cu, Fe and Zn, the subsurface samples were found to have significantly greater variance than the surface samples (Table 4.15). These metals are seen to exhibit **F** values greater than 2.23 which is the critical acceptance value for the null hypothesis (ie. $P = 0.1$) at 11 degrees of freedom. Iron was found to have a particularly high **F** value (12.26). In contrast the **F** value calculated for Pb was relatively low, indicating that the variance of Pb at each depth is not significantly different (Table 4.15).

Although the variance between 0.1M HCl Cu data were significantly different between the surface and subsurface samples, the variance between the corresponding Fe fractions were not significantly different (Table 4.15)

Table 4. 15 Student’s **t**-test and **F**-test statistical data for grid sampling sites 1 to 12.
H₀1 is null hypothesis that there is no difference in the variance of surface and subsurface samples
and H₀2 is the null hypothesis that there is no difference between the means
of the data sets (0-100 mm and 100-200 mm samples).

Metal	Variance		F	Probability of H ₀ 1	<i>t</i>	Probability of H ₀ 2
	0-100 mm	100-200 mm				
Cu (HCl)	0.11	0.37	3.34	$P < 0.05$	-2.89	$P < 0.01$
Fe (HCl)	0.04	0.07	1.90	$P > 0.1$	-3.08	$P < 0.01$
Cu (total)	0.06	0.20	3.45	$P < 0.05$	-2.24	$P < 0.05$
Fe (total)	0.01	0.13	12.26	$P < 0.001$	-1.19	$P > 0.1$
Pb (total)	0.09	0.11	1.18	$P > 0.1$	-0.16	$P > 0.1$
Zn (total)	0.05	0.157	2.85	$P < 0.05$	-2.40	$P < 0.05$

¹³ If the variances of two data sets are significantly different one can hypothesis that the two data sets were drawn from different parent populations.

To assess whether or not the difference in mean metal concentrations between the 0-100 and 100-200 mm samples were significantly different Student's *t*-tests were conducted. Since the *t*-test is sensitive to variance, the *F*-test results were used to identify data sets of equal or unequal variance (Brooks, 1983). With the exception of Pb the *t*-tests were conducted on the logarithms of the elemental 'total' metal concentrations as most of the data was strongly log-normally distributed.

The *t*-test results indicate that there is no significant difference ($P > 0.1$) between the mean total Fe concentrations in the surface (0-100mm) and subsurface (100-200 mm) samples. Similarly the difference between the mean 'total' Pb level in the surface samples was not significantly different to the mean level in the subsurface samples. Mean concentrations of Cu and Zn, however, were found to be significantly different ($P < 0.05$) between the two sampling depths (Table 4.15). The lack of significant difference between the mean Fe concentrations of each depth, is believed to reflect the highly variable Fe content of the tailings, particularly at the 100-200 mm sampling depth (Table 4.15).

Highly significant ($P < 0.01$) differences between the mean concentrations of 0.1M HCl extractable metal concentrations in the surface and subsurface tailings were identified for both Cu and Fe.

Regression analyses were conducted to identify possible correlation between the respective metal concentrations at each depth. An assumption made in conducting the regressions was that depth was an independent variable. Because the Pearson correlation coefficient only provides a valid estimate of the association between two variables if the data is approximately normally distributed, log-normally distributed data was again transformed logarithmically prior to regression analysis (Brooks, 1983).

Results presented in Table 4.16 indicate that in the case of total Cu, Fe, Pb, and Zn that the relationship between surface and subsurface values was either possibly significant ($P < 0.1$) or not significant ($P > 0.1$). A significant relationship ($P < 0.05$) between the two depths was only identified for 0.1M HCl Cu concentrations.

Table 4.16 Relationship between 0-100 and 100-200 mm tailings samples at grid sampling sites 1 to 10. Where H_0 is the null hypothesis that there is no relationship between metal concentrations in the respective layers. (r = Pearson correlation coefficient; degrees of freedom = 10)

Metal	r^2	Probability of H_0
Cu (HCl)	0.42	$P < 0.05$
Cu (total)	0.11	$P > 0.1$
Fe (HCl)	0.02	$P > 0.1$
Fe (total)	0.04	$P > 0.1$
Pb (total)	0.33	$P < 0.1$
Zn (total)	0.26	$P < 0.1$

4.3.5.2 0.1M HCl Extractable

Predictably 0.1M HCl extractable metal concentrations were generally much lower than 25 % HNO_3 extractable levels (Table 4.14). This indicates that the majority of Cu and Fe is not in a form readily available to plants. The average concentrations of 0.1M HCl extractable Fe in both the 0-100 mm and 100-200 mm sampling zone were greater than those of copper. As a percentage of the total Fe in the tailings, however, the concentrations of Fe extracted by 0.1M HCl was relatively low in the surface tailings (Table 4.13).

Figure 4.14b indicates that there is no significant relationship between the total and 0.1M HCl extractable Fe concentrations in the 100-200 mm tailings and only a possibly significant ($P < 0.1$) relationship between the fractions at 0-100 mm depth. A line fitted to non-logarithmically-transformed 0-100 mm Fe concentration data indicates that 0.1M HCl extracts approximately 3% of the total Fe in the surface tailings (Figure 4.15b). The justification for treating the 0-100 mm and 100-200 mm samples separately is based on the fact that the mean concentrations of the samples' 0.1M HCl extractable Fe and Cu were significantly different (Table 4.15).

In the case of Cu, a far 'better' relationship ^{was found} between the 'total' and 'labile' Cu concentrations in the grid samples at both depths (Figure 4.14a). In contrast to Fe, the relationship between the two Cu fractions was found to improve with depth. Based on the slope of the line fitted to the non-transformed concentration data it is evident that a

greater proportion of Cu is extractable by 0.1M HCl in the subsurface samples (31%) than in the surface samples (18%) (Figure 4.15a). These results confirm findings discussed in Chapter 4.3.5.2 which indicate that a larger proportion of the ‘total’ Cu in the tailings is extracted by 0.1M HCl extraction procedure.

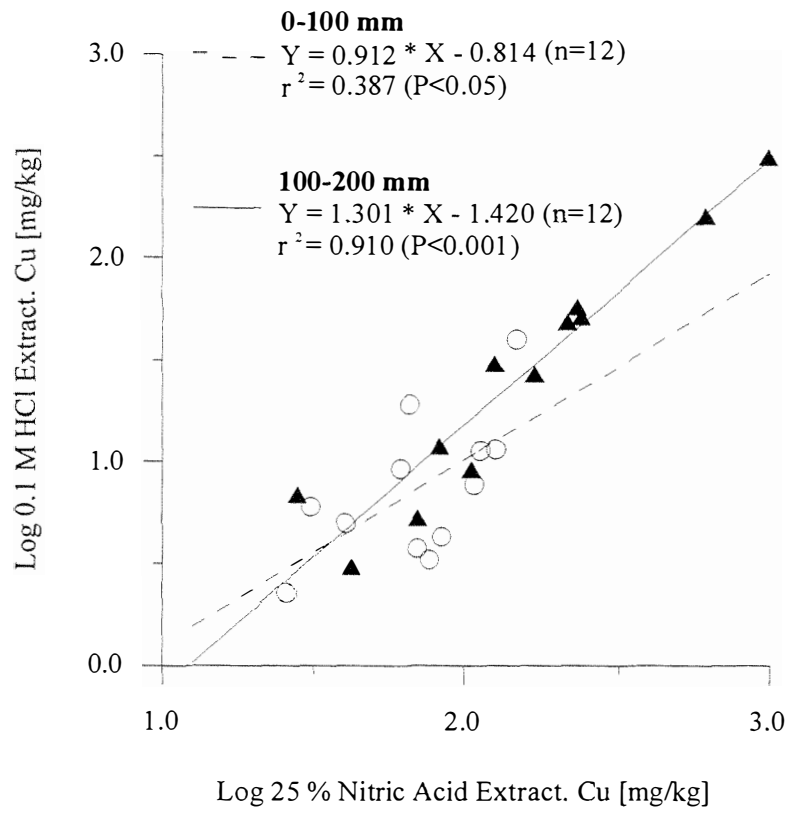
Figures 4.16 & 4.17 show the spatial variability of 0.1M HCl extractable Cu and Fe in the surface and subsurface samples. As confirmed by regression analysis discussed in the previous section, Cu levels show similar spatial trends at both depths.

4.3.5.3 Discussion on Metal Concentrations

Although the differences in mean ‘total’ Fe concentrations between the upper and lower sampling zones were non-significant, it is postulated that the weathering of the surface tailings (0-100mm) has resulted in a general reduction in both the concentrations and variability of total Cu, Fe and Zn within this zone. The much lower range of these metal concentrations in the surface (0-100 mm) tailing is postulated to reflect better aeration and hence more thorough oxidation of the surface tailings (Table 4.14).

Despite the fact that concentrations of 25% HNO₃ extractable Cu and Fe generally tended to be slightly higher at the western end of the dam (Figure 4.1), Cu and Fe concentrations within surface 200 mm of the profile appear to be randomly distributed (Figures 4.18 and 4.19). Environmental factors such as the variable water-table height about the dam, thus appear to have had little influence on the oxidation of Fe and Cu-bearing sulphide minerals within the surface 200 mm of the tailings.

Total Zn concentrations also appeared to be randomly distributed in the surface and subsurface tailings samples (Figure 4.20). Both the surface and subsurface HNO₃ extractable Pb concentrations, however, were found to generally increase towards the western end of the dam (Figure 4.21). A significant ($P < 0.05$) and a possibly significant ($P < 0.1$) inverse relationship were identified between the total Pb concentrations and tailings pH in the 0-100 mm and 100-200 mm sampling zones respectively (Figures 4.22). As reported in Chapter 6 a similar relationship between pH and 0.1M HCl



(b)

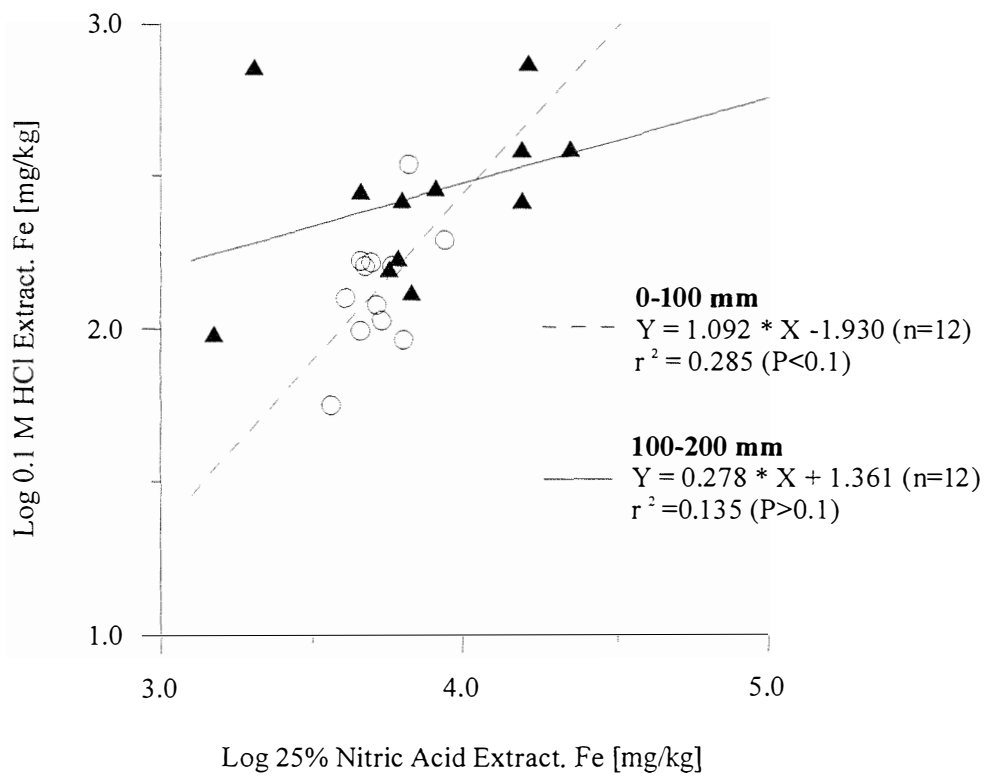


Figure 4.14 (a) Log 0.1M HCl Cu versus Log 'Total' Cu and (b) Log 0.1M HCl Fe versus Log 'Total' Fe
 Separate correlations are shown for individual depths (0-100 mm and 100-200 mm).

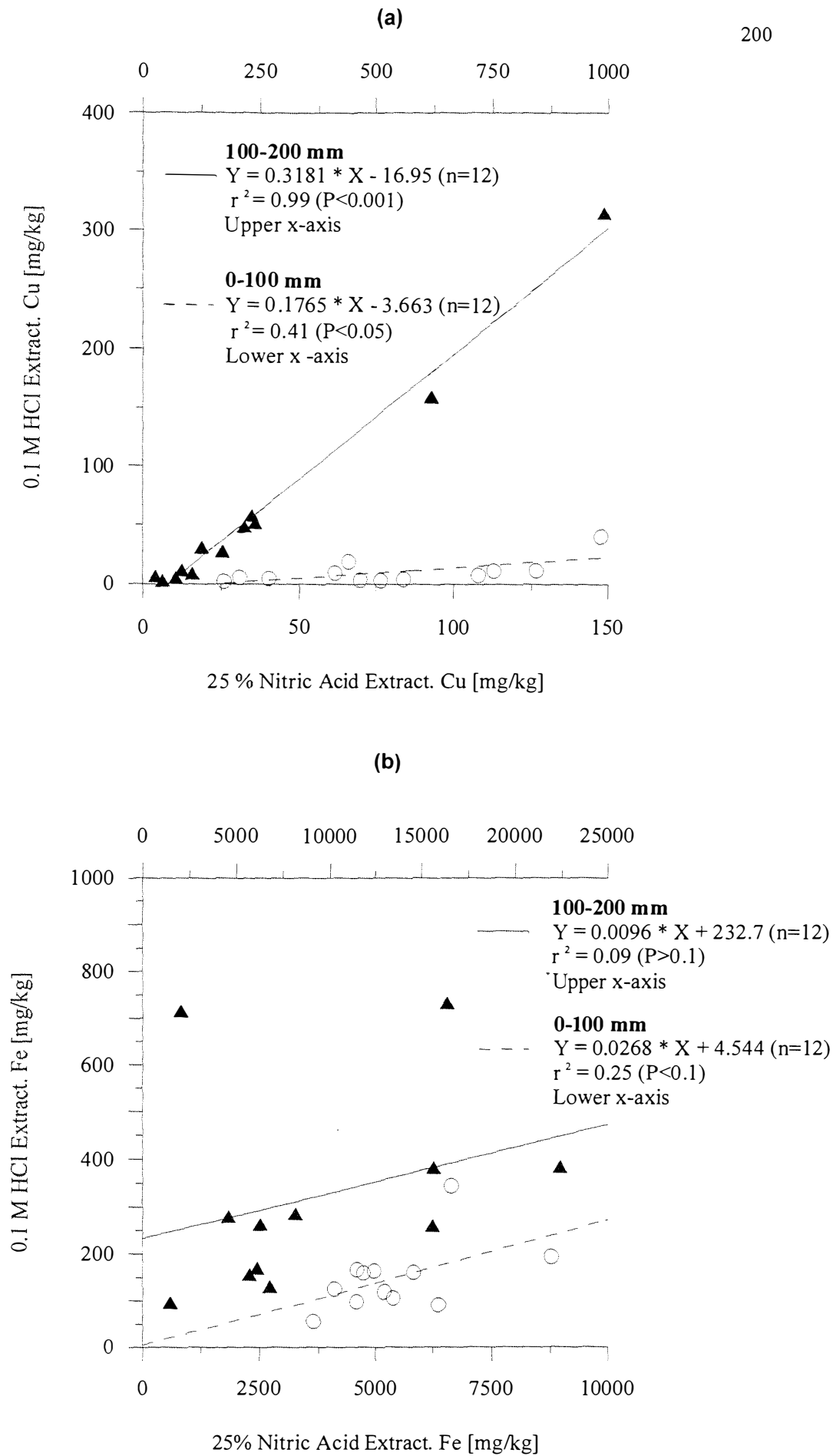


Figure 4.15 (a) 0.1 M HCl Cu versus 'Total' Cu and (b) 0.1M HCl Fe versus 'Total' Fe
Separate correlations are shown for individual depths (0-100 mm and 100-200 mm).

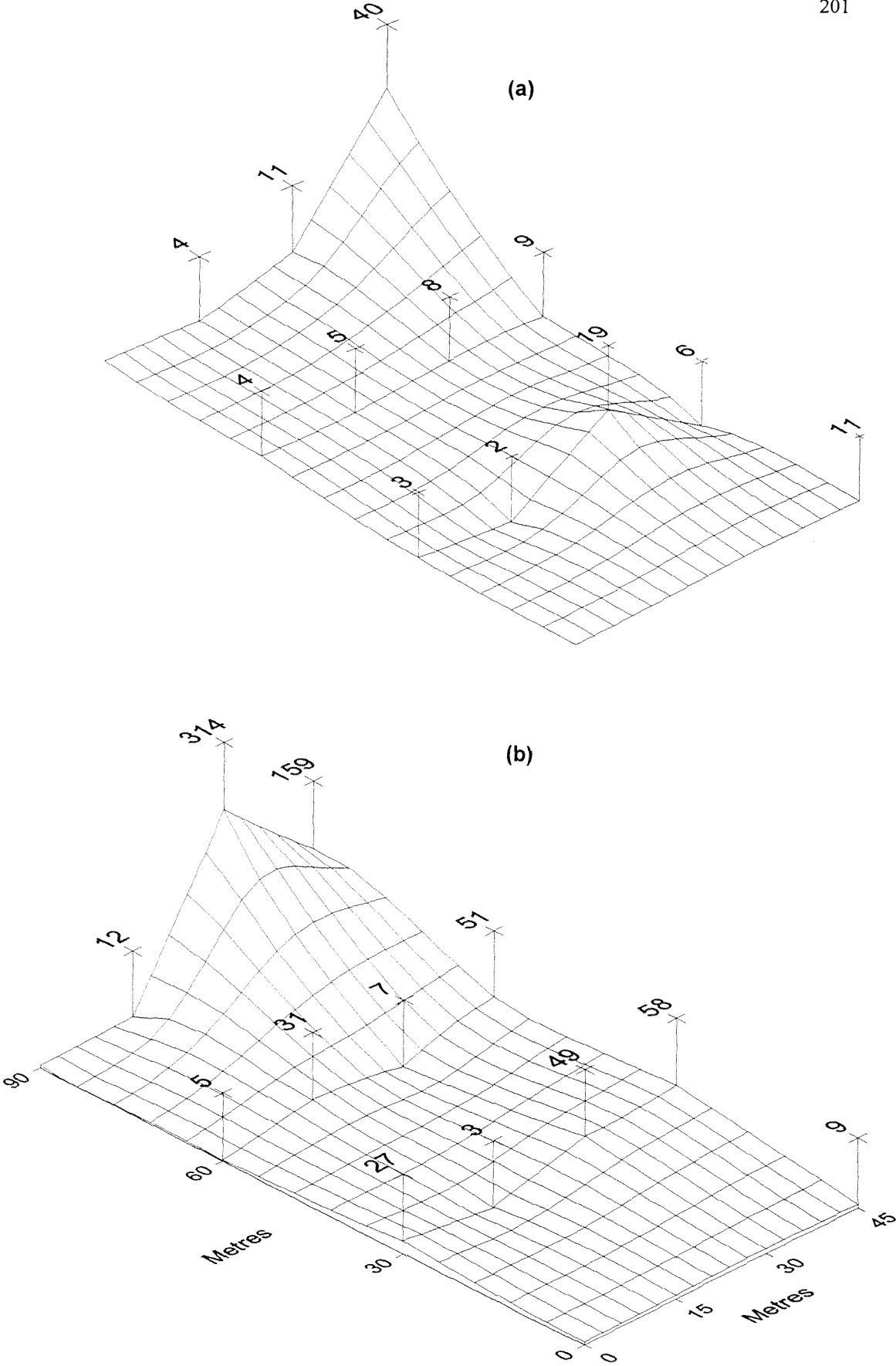


Figure 4.16 0.1M HCl extractable Cu concentrations [mg/kg] in (a) 0-100 mm zone and (b) 100-200 mm zone.

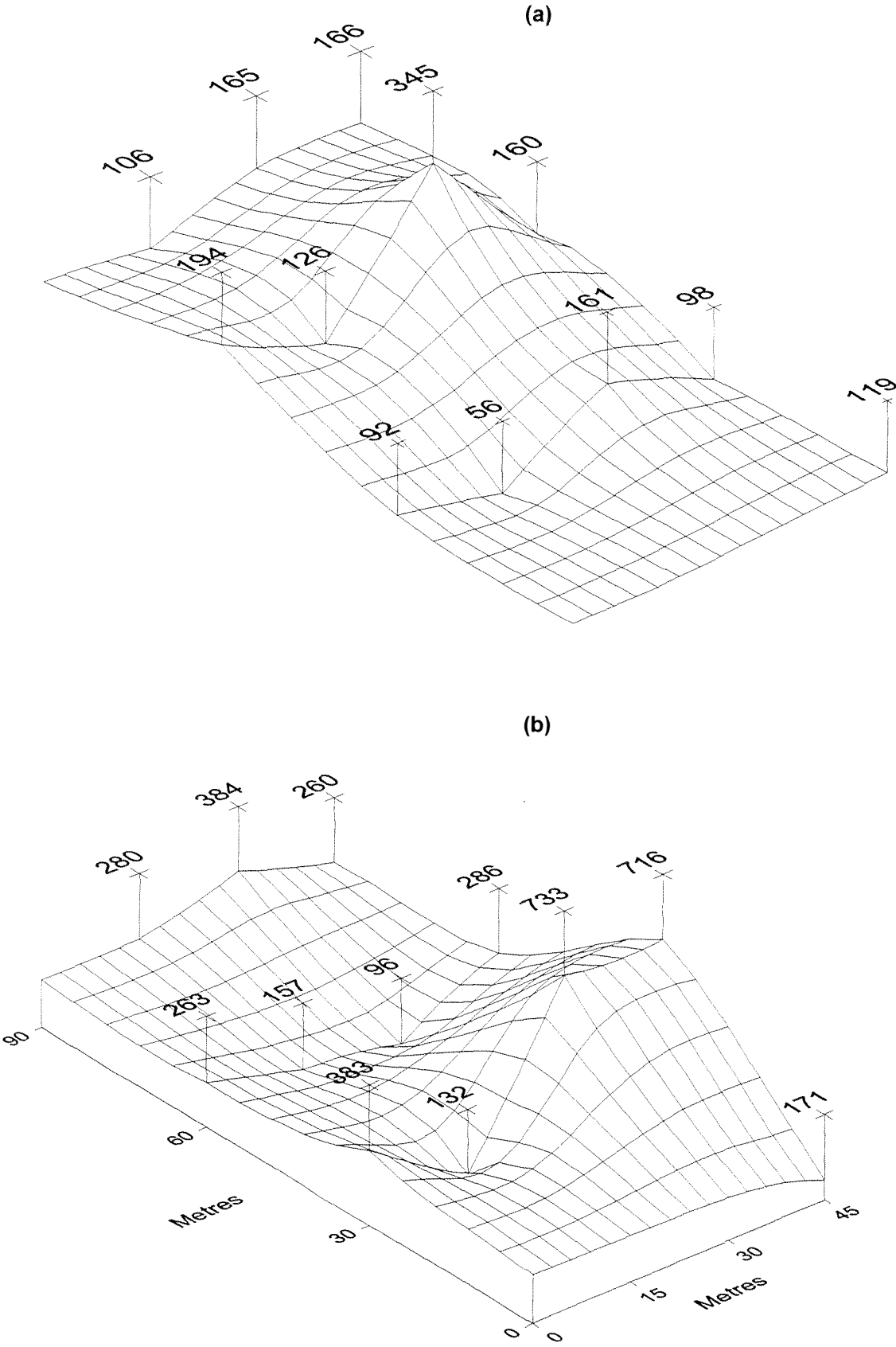


Figure 4.17 0.1M HCl extractable Fe concentrations [mg/kg] in (a) 0-100 mm zone and (b) 100-200 mm zone.

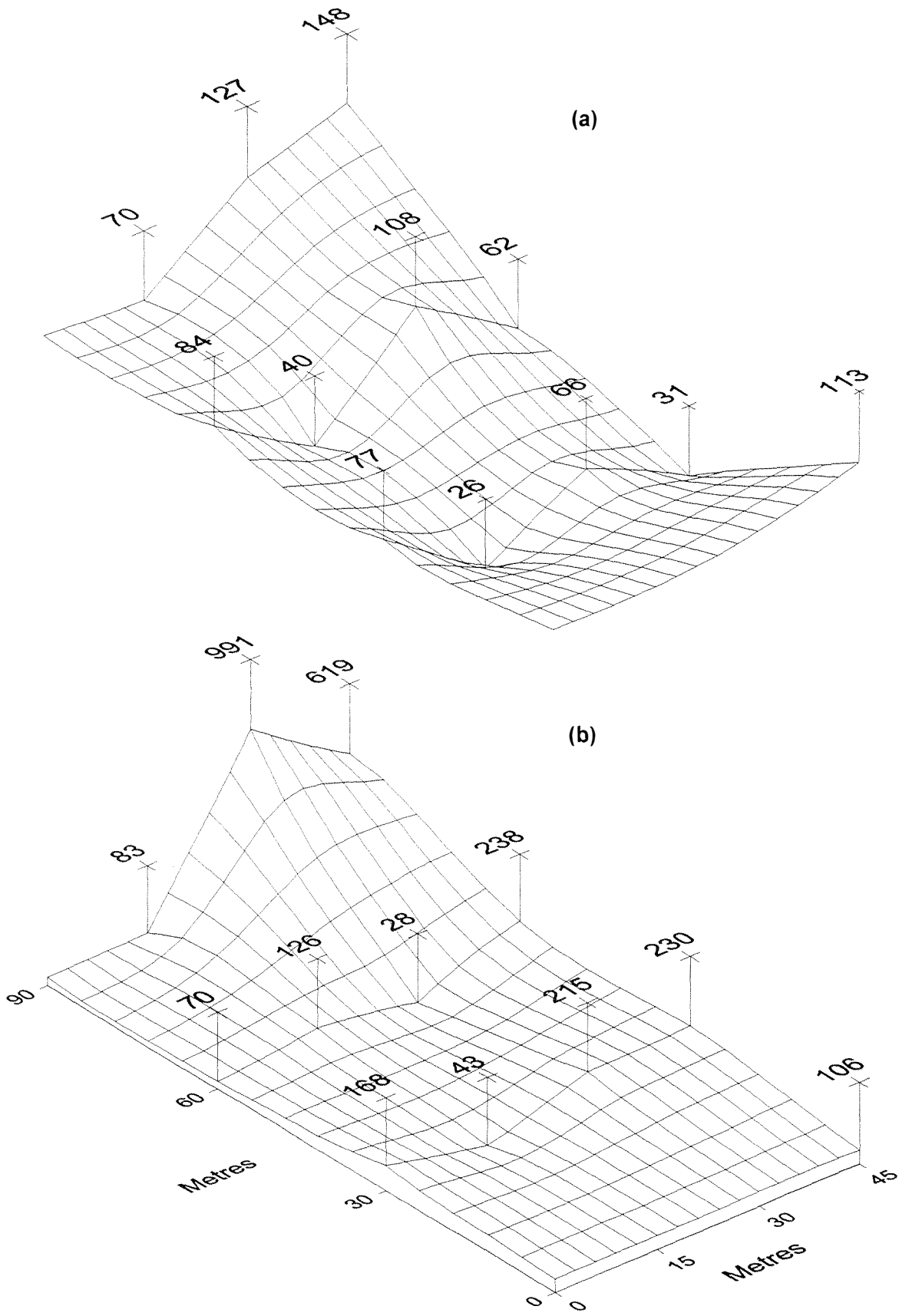


Figure 4.18 'Total' extractable Cu concentrations [mg/kg] in (a) 0-100 mm zone and (b) 100-200 mm zone.

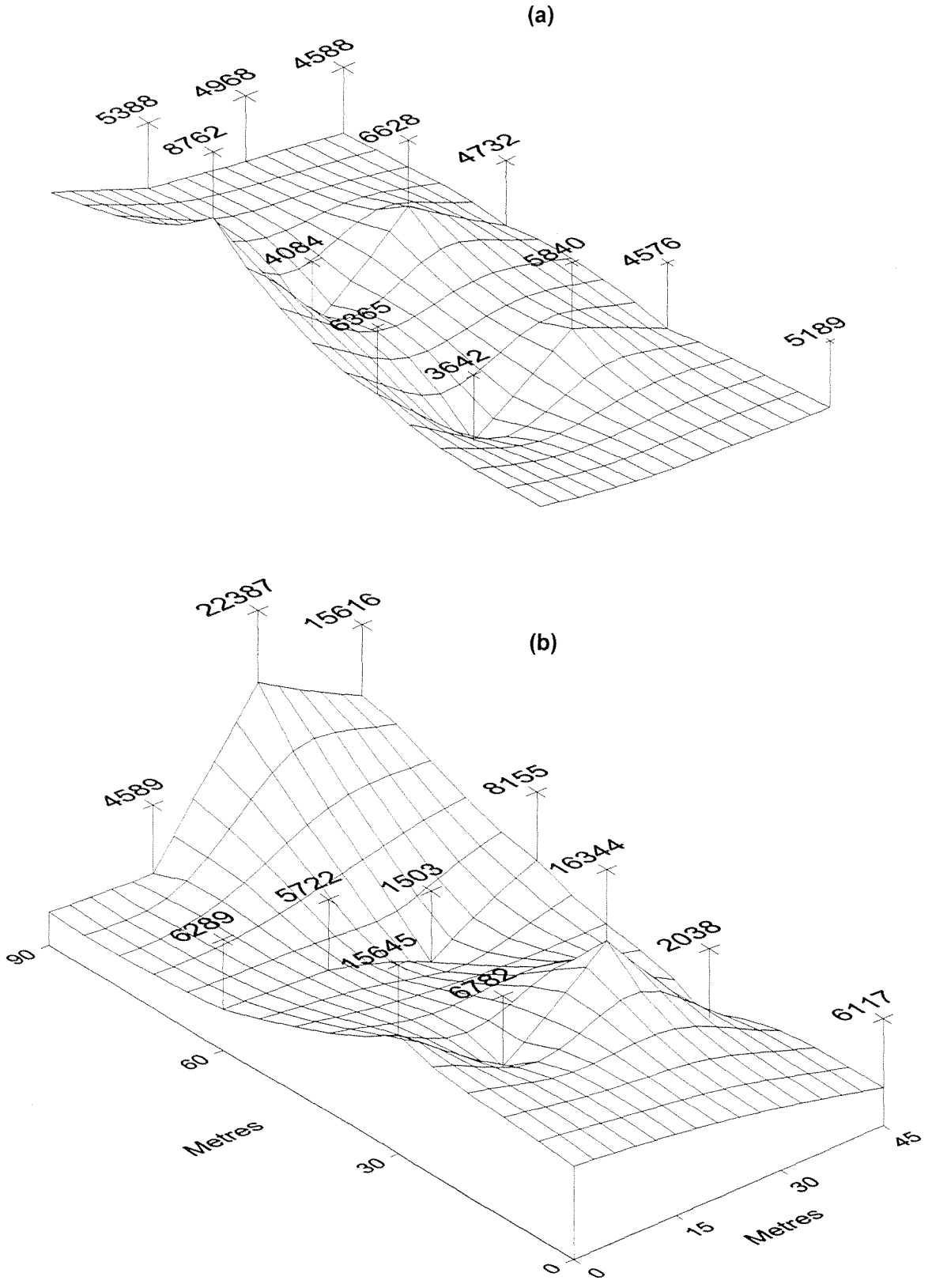


Figure 4.19 'Total' extractable Fe concentrations [mg/kg] in (a) 0-100 mm zone and (b) 100-200 mm zone.

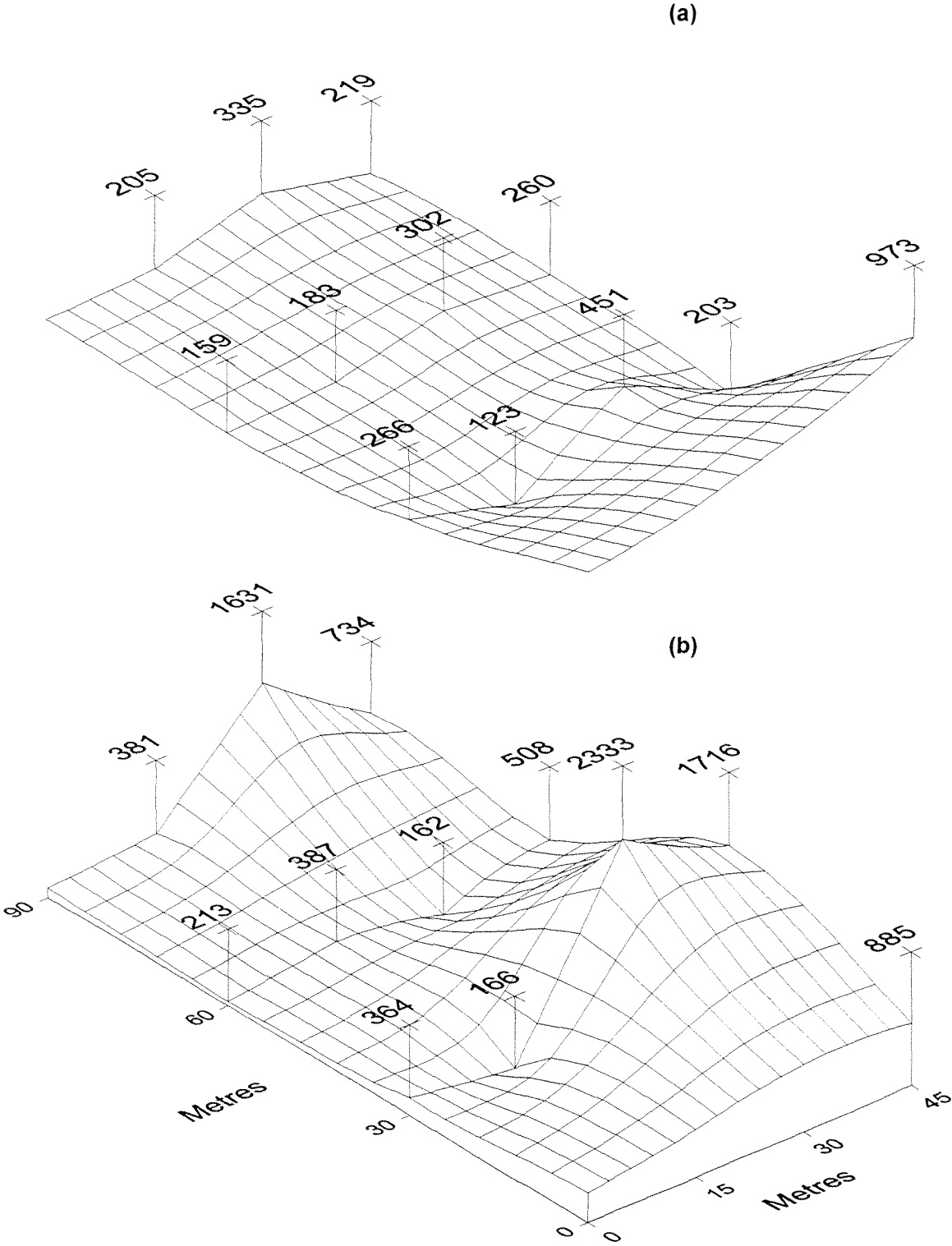


Figure 4.20 'Total' extractable Zn concentrations [mg/kg] in (a) 0-100 mm zone and (b) 100-200 mm zone.

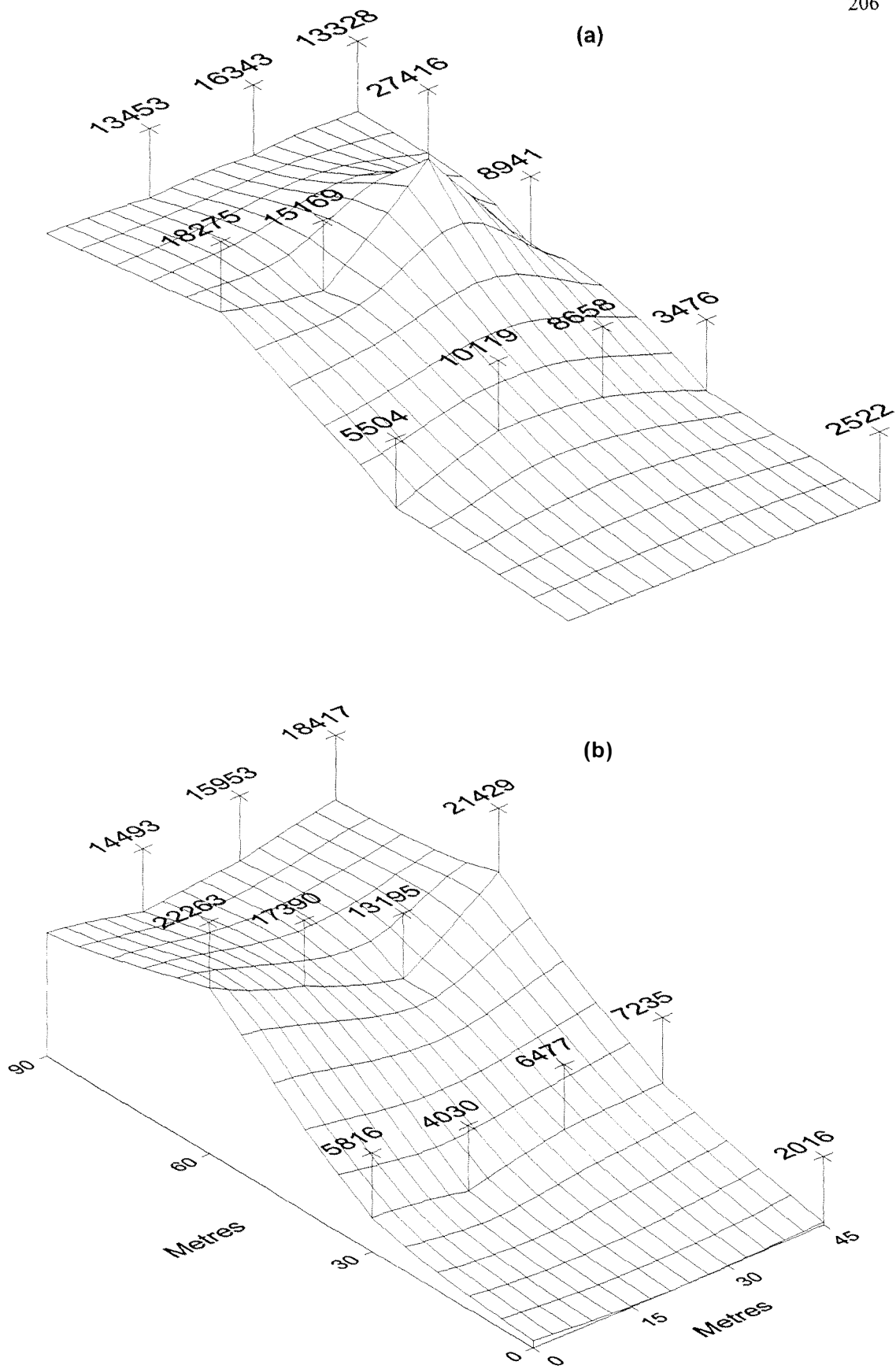


Figure 4.21 'Total' extractable Pb concentrations [mg/kg] in (a) 0-100 mm zone and (b) 100-200 mm zone.

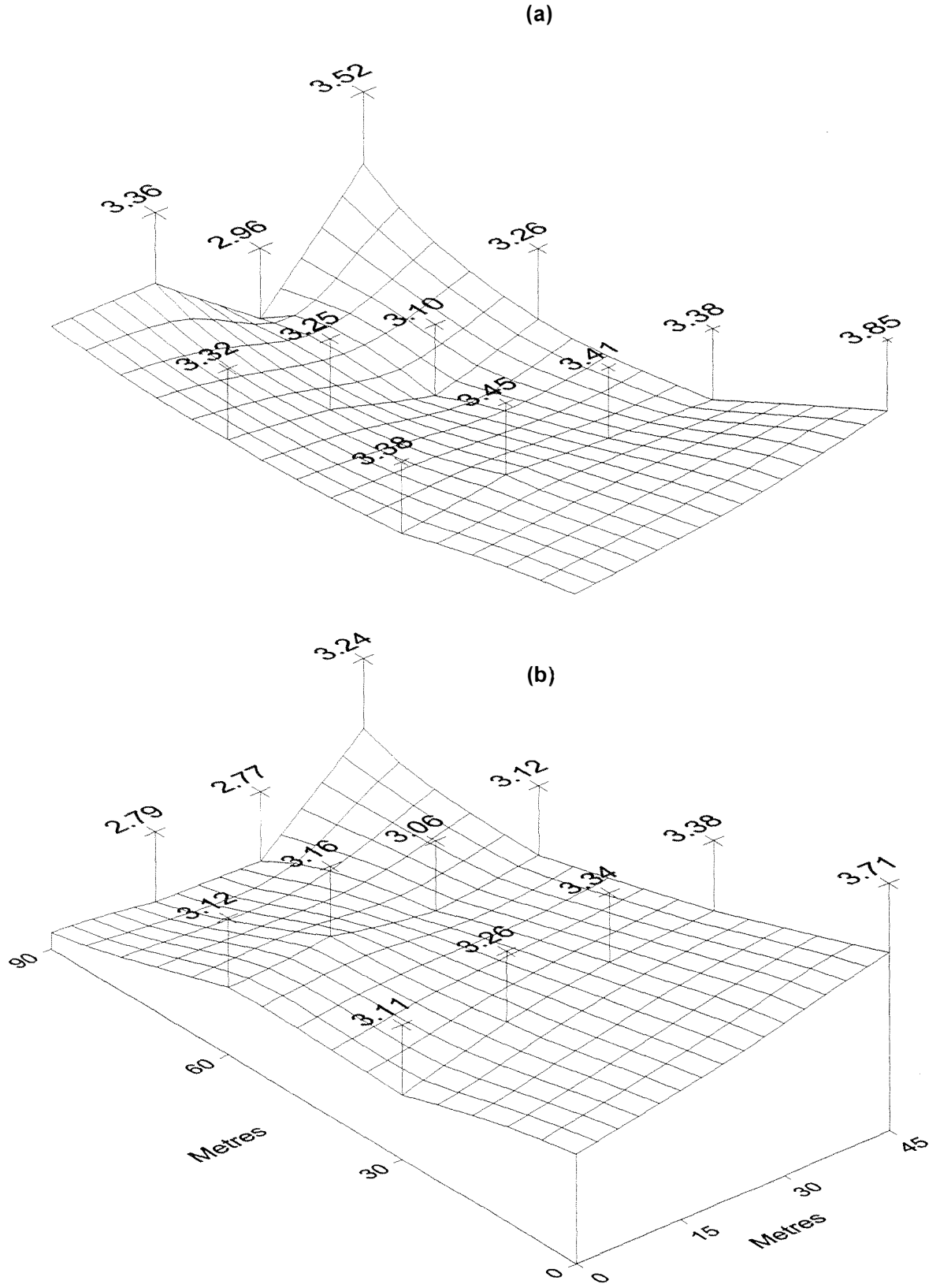


Figure 4.22 Mean pH levels in (a) 0-100 mm zone and (b) 100-200 mm zone.

extractable Pb was identified in incubated samples. Whilst the relationship in Chapter 6 was potentially explained by the increased activity of $\text{SO}_4^{=}$ decreasing the solubility of Pb present as PbSO_4 , the negative correlation between 'total' Pb and pH is not readily so explained.

One observation that indicates that Pb may have been preferentially leached from the surface tailings at the eastern end of the dam is that this area coincides with the region of the dam (sites 2,5,8, and 11) where the water-table is known to frequently penetrate the surface tailings (Chapter 4.2.2.1). It is possible that Pb has been very gradually depleted as a result of PbSO_4 dissolution under the geochemical conditions prevailing at these sites. Presumably low pH conditions may similarly reflect leaching of acidic oxidation products in this region of the dam. Further discussion of the spatial variability of pH is reported in section 4.3.6.5.

4.3.6 Sulphur & pH Characterisation

Preliminary characterisation of the Tui mine tailings reported in Chapter 4.1 indicated that the tailings contain extremely high concentrations of non-organic sulphur. Total S and $\text{SO}_4^{=}$ concentrations were both found to increase dramatically with depth. To further investigate these trends the concentrations of total S and $\text{SO}_4^{=}$ were determined in 32 samples obtained from grid sampling sites 7 and 9. Sampling was conducted at 50-mm intervals.

4.3.6.1 Total Sulphur

Analytical results indicate that the concentrations of total S at each site are comparable and vary in a similar fashion down the profiles (Figure 4.23). Although the surface tailings were found to contain relatively low concentrations of sulphur, levels in excess or approaching 40,000 mg/kg were encountered at both sites within 250 mm of the surface (Figure 4.23). At site 7 total sulphur concentrations were found to remain relatively constant beneath this depth, varying between about 30,000 and 45,000 mg/kg (Figure 4.23a). Subsurface sulphur concentrations at site 9, however, were more variable and ranged from about 22 000 mg/kg at 400-450 mm depth to nearly 56 000 mg/kg at 650-700 mm depth (Figure 4.23b).

Total sulphur concentrations in the bulk samples were comparable to the levels obtained in the corresponding incremental samples and again indicate that the surface tailings contain relatively low concentrations of sulphur (Figure 4.23).

4.3.6.2 Phosphate Extractable Sulphate

With the exception of a few samples at site 7, the incremental samples were all found to contain very high levels of $\text{SO}_4^{=}$ compared to most New Zealand soils which typically contain between 15 and 50 mg/kg of phosphate extractable $\text{SO}_4^{=}$ (Blakemore *et al.*, 1987). In a similar fashion to total sulphur, $\text{SO}_4^{=}$ concentrations in the tailings were also found to vary substantially with depth (Figures 4.24). Sulphate levels at site 7 for example, varied from less than 10 mg/kg to over 1400 mg/kg. Although substantially higher concentrations of $\text{SO}_4^{=}$ were found in the surface tailings at site 9, maximum levels throughout the profile at this site did not exceed 1000 mg/kg (Figure 4.24b).

Figure 4.24 indicates that $\text{SO}_4^{=}$ concentrations were found to peak at about 200 mm depth at both sites and were generally highest in the central region of the profiles between about 200 and 400 mm depth.

In accordance with $\text{SO}_4^{=}$ levels in the incremental samples, concentrations in the bulk samples were also found to be greater in the subsurface (150-300 mm) samples at both sites 7 and 9. The concentrations of $\text{SO}_4^{=}$ in the bulk samples, however, were substantially higher than those found in the incremental samples of corresponding depths. This was particularly evident at site 9 where $\text{SO}_4^{=}$ concentrations in both the surface (0-150 mm) and subsurface bulk samples exceeded the maximum $\text{SO}_4^{=}$ level found in any of the site's incremental samples (Figure 4.24).

4.3.6.3 pH Variation with Depth

To elucidate the trends observed at preliminary sampling sites S1, S2 and S3, the pH of 22 samples from site 7 and 16 samples from site 9 were determined. Incremental sampling as described in Chapter 4.3.1.2 was again conducted at 50-mm intervals to 1000 mm and 800 mm depths at sites 7 and 9 respectively. At site 7 an additional two samples were collected between 1000 and 1300 mm.

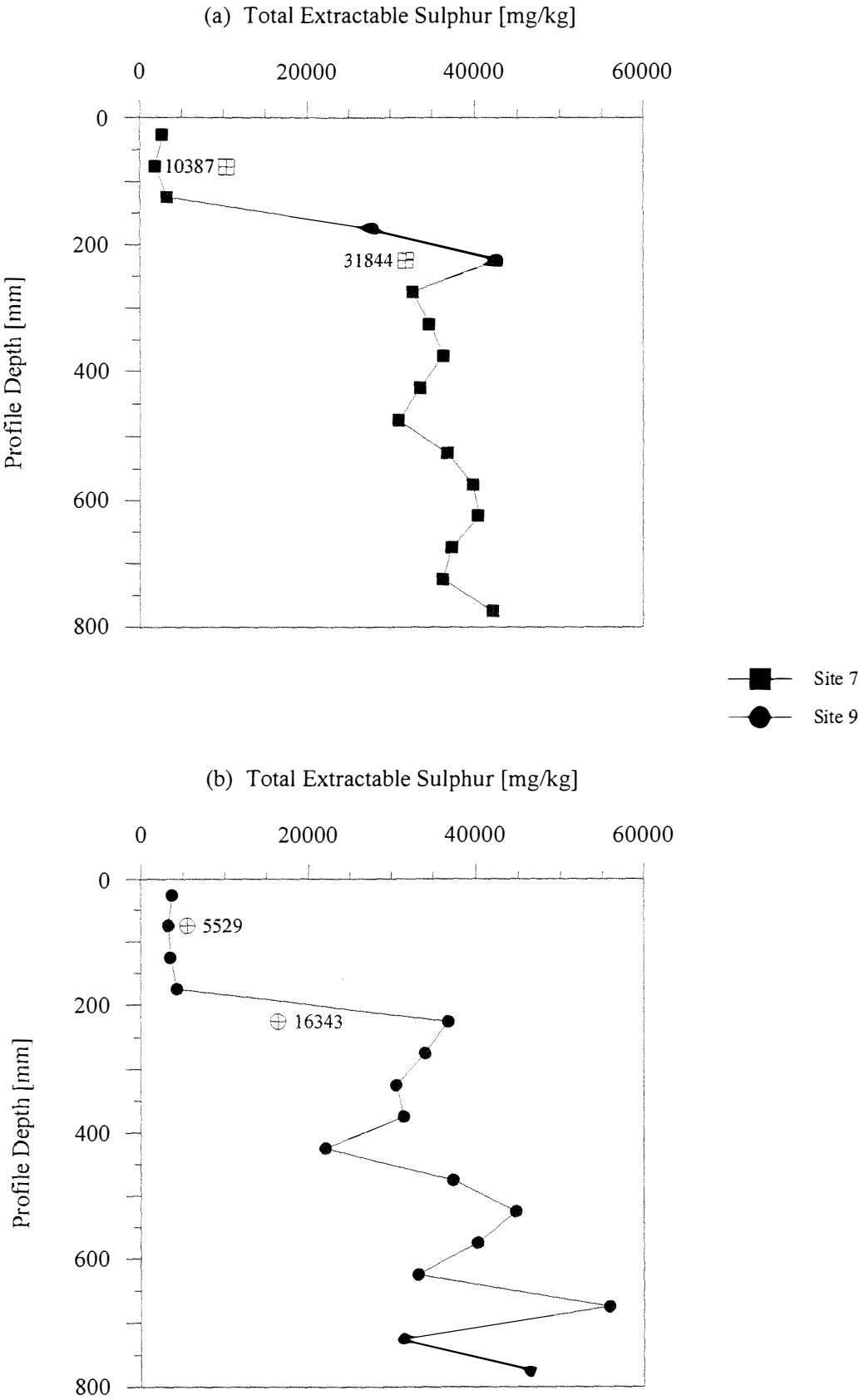


Figure 4.23 Total extractable sulphur versus depth at (a) grid sampling site 7 and (b) grid sampling site 9.

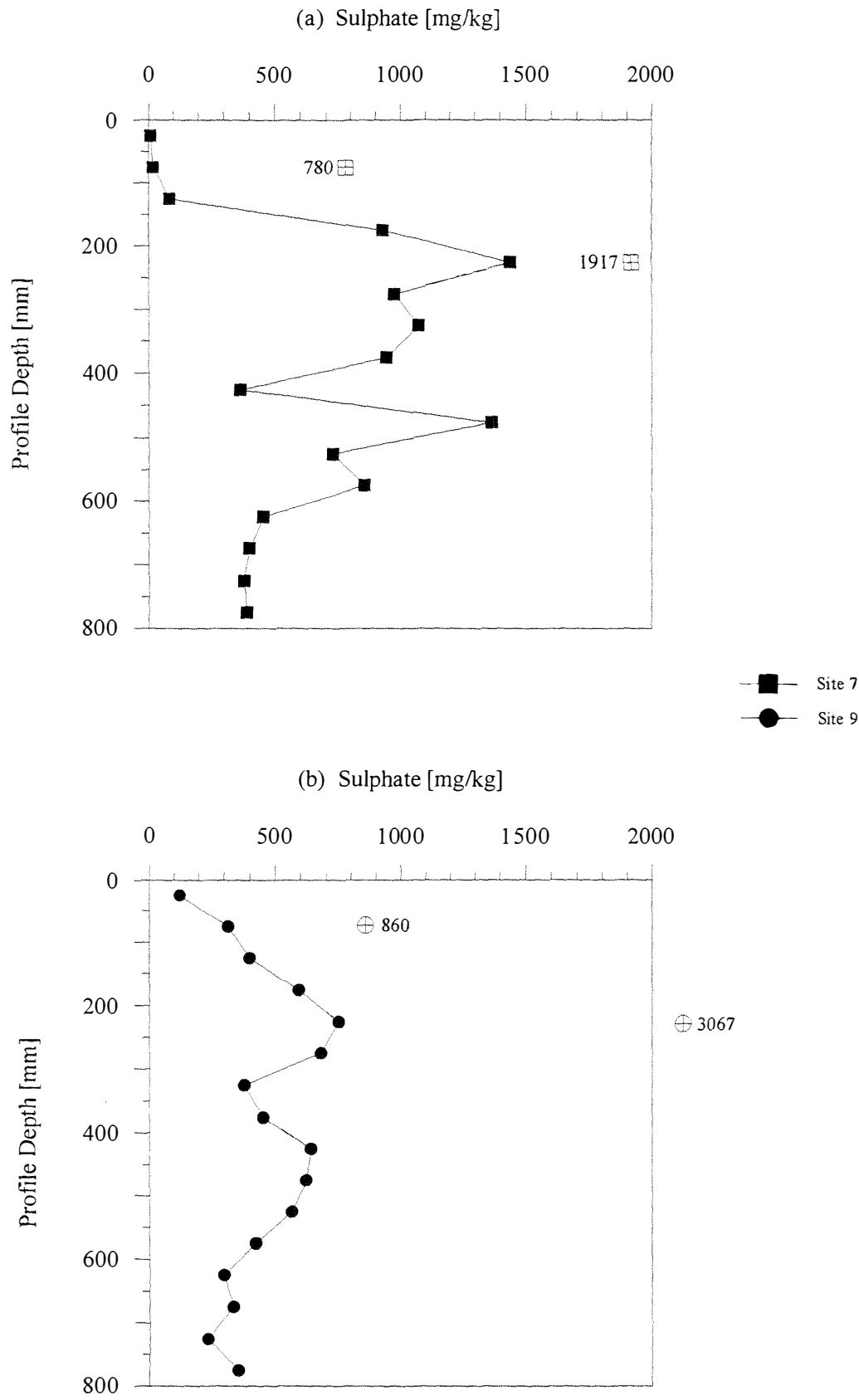


Figure 4.24 Phosphate extractable sulphate versus depth at (a) grid sampling site 7 and (b) grid sampling site 9.

The tailings at these sites were found to exhibit similar pH profiles (Figure 4.25) that were comparable to those obtained from the 3 preliminary sampling sites (Figure 4.3b). pH values at sites 7 and 9 were found to vary from about pH 4 in the uppermost samples to less than 2.5 between 150 and 250 mm depth, to approximately 6 below 600 mm depth. Profile pH minima of 2.14 and 2.45 were obtained for sites 7 and 9 respectively at approximately 200 mm depth. Below this depth the pH of the tailings was found to gradually increase to reach about pH 6 at 600 mm depth. Only a very slight rise in pH was noted further down the profile (Figure 4.25).

4.3.6.4 pH/Sulphate Correlation

When the incremental pH values of each site were plotted against $\text{SO}_4^{=}$ concentrations, it became evident that the zones of low pH coincided with $\text{SO}_4^{=}$ maxima within the profiles (Figures 4.26). The respective pH minima and $\text{SO}_4^{=}$ maxima were found to occur between 150 mm and 250 mm depth at both sites which indicates that the majority of sulphide oxidation may be taking place within this depth zone at both sites.

Although regression analysis indicated a possible relationship existed between pH and $\text{SO}_4^{=}$ at site 7, no significant relationship between the two parameters was found to exist at site 9. A highly significant ($P < 0.01$) linear relationship between tailings pH and $\text{SO}_4^{=}$ concentrations was, however, achieved when the surface 3 samples at each site were removed from the regression (Figure 4.27). It is considered that the removal of this data from the regression calculations was justified because upon plotting pH against $\text{SO}_4^{=}$ concentrations it was noted that these samples (25, 75, 125 mm) exhibited disproportionately low sulphate concentrations (Figures 4.27). The low $\text{SO}_4^{=}$ concentrations are attributable to strong leaching of $\text{SO}_4^{=}$ under acidic conditions induced by sulphide oxidation. This finding is consistent with lyotropic series that indicate that the rate of adsorption of hydrogen ions (H^+) is much higher than that of the divalent sulphate anions ($\text{SO}_4^{=}$) (Tan, 1993). Hydrogen ions are exceptional in that they are more strongly adsorbed than other monovalent and divalent cations. Positive adsorption of $\text{SO}_4^{=}$ on the other hand is comparably low. Thus in a solution containing ions such as Fe^{2+} , Zn^{2+} and H^+ , sulphate mobilisation is usually controlled by the formation of highly soluble metal compounds rather than due to complexation with H^+

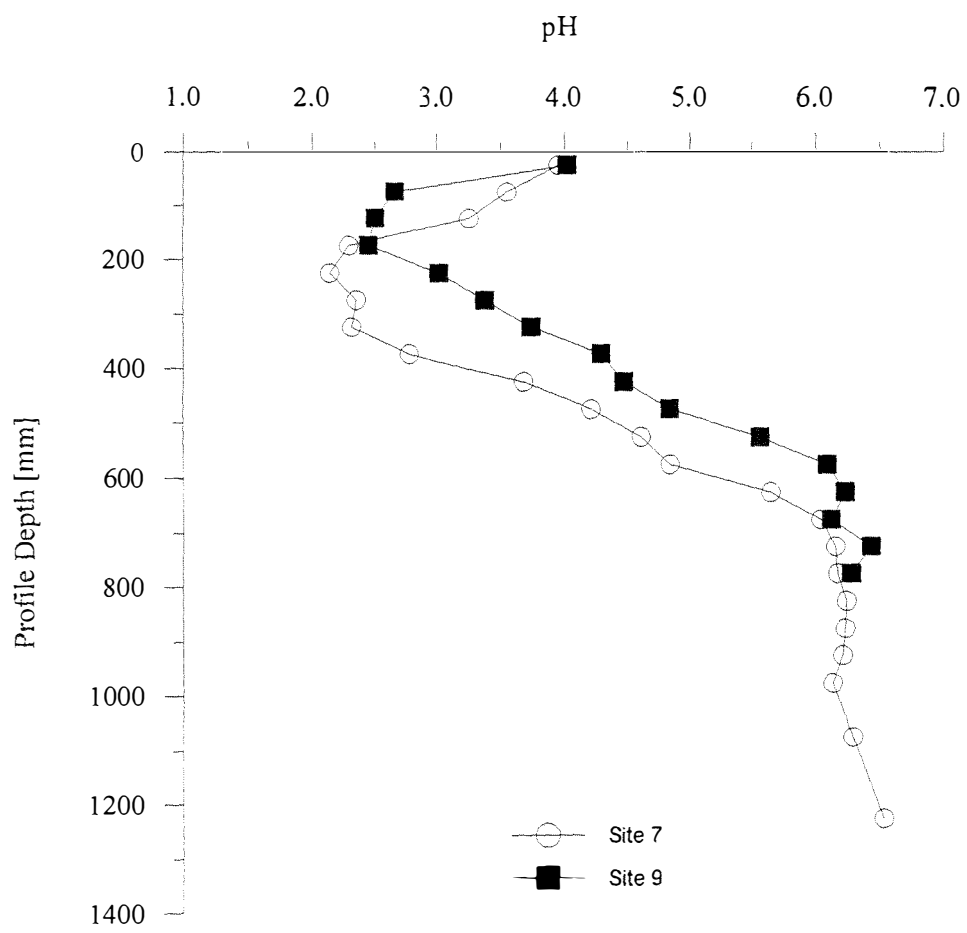


Figure 4.25 Mean pH versus depth at grid sampling sites 7 and 9.

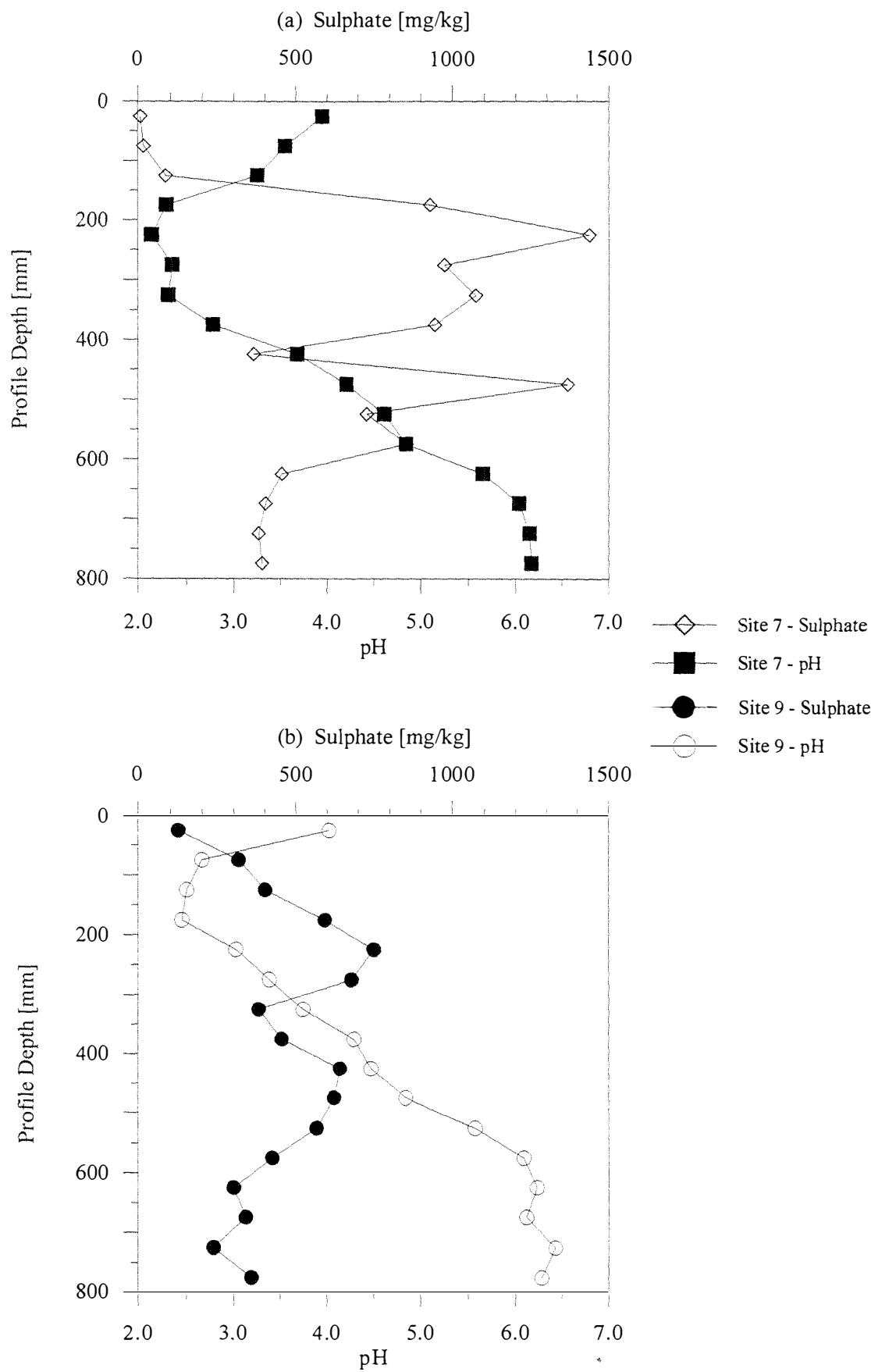


Figure 4.26 Phosphate extractable sulphate and pH versus depth at (a) grid sampling site 7 and (b) grid sampling site 9.

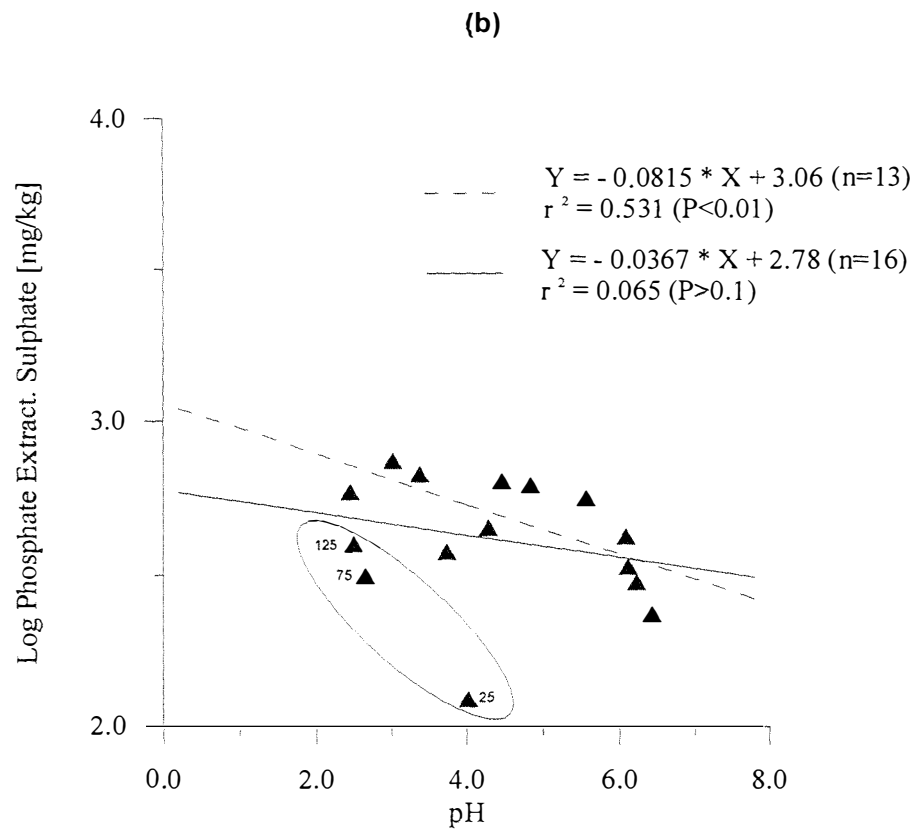
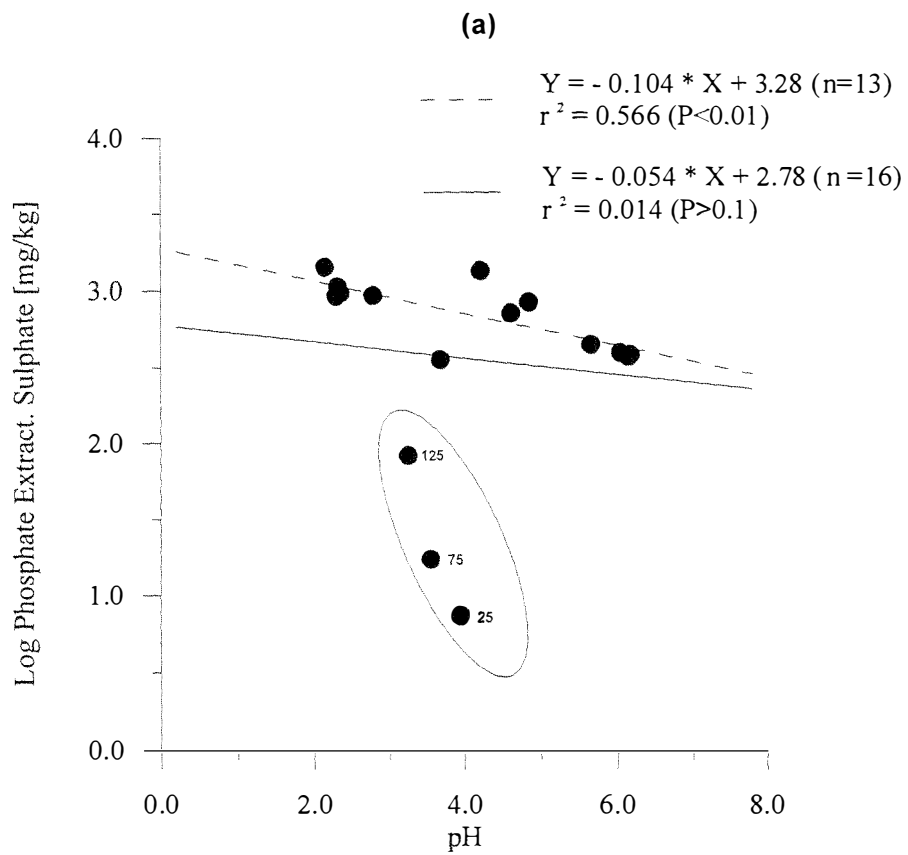


Figure 4.27 Log Phosphate extractable sulphate versus pH at (a) grid sampling site 7 and (b) grid sampling site 9
Correlation was conducted both with and without the uppermost 3 surface samples.

(Tan, 1993). The relative mobility of H^+ and $SO_4^{=}$, thus explains the relationship between these two parameters and depth.

Previous studies investigating the reclamation of pyritic mining wastes have also identified linear relationships between pH and sulphate concentrations (Pulford & Duncan, 1978; Arora *et al.*, 1979). Pulford & Duncan (1978) used this relationship in an attempt to predict the acid generating potential of coal-mine wastes originating from Central Scotland. Their research indicated that samples from the same site, or samples from different sites of similar age tended to have uniform pH and sulphate levels, and that the method was potentially useful for assessing the relative reactivity of pyrite-bearing mine wastes.

4.3.6.5 Spatial pH Variation

In addition to assessing the variation of pH with depth at sampling sites 7 and 9, duplicate pH determinations were conducted on the surface (0-100 mm) and subsurface (100-200 mm) samples at each of the 12 grid sites. All of the grid samples exhibited acidic pH which ranged from 2.77 to 3.85 (Table 4.17). At all bar one of the 12 sampling sites, the pH of the surface tailings was greater than that of the subsurface samples. The only site not to demonstrate this trend (site 2) exhibited a pH of 3.38 in both the surface and subsurface tailings (Figures 4.22).

Table 4.17 Average pH values and range for grid sampling sites 1 to 12. pH values of the grid samples and bulk samples (bracketed data) are also included for sites 7 and 9.

Depth [mm]	Average pH	Range	Site 7	Site 9
0-100 (0-150)	3.35 ± 0.21	2.95 - 3.85	2.96 (2.50)	3.25 (2.44)
100-200 (150-300)	3.17 ± 0.25	2.76 - 3.73	2.77 (2.68)	3.16 (2.11)

An **F**-test conducted on the two groups of data indicated that there was no significance difference between the variance of the surface and subsurface tailings (Table 4.16). A significant difference ($P < 0.05$) was noted, however, between the means of the samples

(Table 4.18). This indicates that at the time of sampling the temporal variation in pH was greater than the spatial variability of the tailings.

Table 4.18 Pearson’s correlation coefficient (*r*), Student’s *t*-test and *F*-test results based on pH data for 0-100 mm and 100-200 mm depths (grid sampling sites 1 to 12).

Variance		F value	t value	r ²
0-100 mm	100-200 mm			
0.05	0.06	1.33 P >0.1	1.88 P < 0.05	0.66 P < 0.01

Regression analysis of the surface and subsurface samples indicates that a highly significant positive relationship between surface and subsurface pH exists (Figure 4.47). No such correlation was identified between the sites’ pH and 0.1*M* HCl or 25% HNO₃ acid extractable Cu and Fe in the tailings at either depth. This finding is consistent with previous studies that have identified other factors such as particle grain size, bacterial populations and oxygen accessibility as being the primary factors controlling sulphide oxidation and hence H⁺ activity within sulphidic mining wastes (Chapter 3, section 3.3.3). A lack of relationship between pH and the concentrations of 0.1*M* HCl Cu and Fe in the tailings is explained by^{the} relative immobility of H⁺ compared to Cu²⁺ and Fe²⁺ which would result in preferential leaching of these metallic cations from the tailings.

Although the bulk samples were found to exhibit comparable pH values to the corresponding incremental samples, the grid samples obtained from sites 7 and 9 were notably less acidic than the bulk samples obtained from the corresponding sites (Table 4.17). The lower pH values obtained from the grid samples is possibly just a result of chemical variability within the tailings dam, however, other factors such as climate induced leaching prior to grid sampling may have reduced sample acidities.

4.3.7 Conclusions on Chemical Characterisation

The 25% (v/v) HNO_3 procedure of Smith & Bradshaw was compared against an HF based extractant and found to adequately estimate the heavy metal contents of the Tui tailings. The procedure was found to dissolve between about 90 and 100% of the total metals within the tailings (Figures 4.8 & 4.9). The HNO_3 extractant was particularly effective at liberating Fe, indicating that a negligible proportion of the Fe is bound within silicate minerals (section 4.3.3.3). In contrast to the 25% HNO_3 procedure, the quantity of metal extracted by the trial H_2O_2 procedure was found to vary substantially between samples. Following H_2O_2 oxidation, comparatively very low levels of Fe and Pb were detected in solution due to the formation of highly insoluble oxidation products (4.3.3.4).

Characterisation of incremental samples at site 7 identified that 25% HNO_3 ('total') Fe levels increased from relatively low concentrations of about 3000 mg/kg in the surface tailings (0-100 mm) to about 50,000 mg/kg at 500-600 mm depth (Figure 4.10a). Copper and Zn levels were much lower than Fe concentrations in the surface tailings but like Fe increased substantially down the profile to reach levels of approximately 2100 and 5400 mg/kg respectively at 400-500 mm depth (Figure 4.11a). The distribution of Pb in the tailings was found to contrast those of Cu, Fe and Zn in that it was found in slightly higher total concentrations near the surface of the profile. Pb concentrations were extremely elevated in the tailings at site 7, ranging from about 11,000 mg/kg to 4000 mg/kg (Figure 4.10a).

With the exception of Cu, 0.1M HCl was generally found to extract less than 10% of the 'total' metals in the tailings indicating that metals are predominantly in the form of sulphide minerals, oxides or highly insoluble sulphates. Below 300 mm depth >50% of the 'total' Cu was extracted by the dilute acid extractant indicating the presences of high concentrations of labile Cu. Like 'total' metal concentrations, 0.1M HCl extractable metal levels were generally found to increase with depth at site 7 (Figures 10b & 11b). Interpretation of grid sampling site data indicates that the positive correlation between 'total' and 0.1M HCl extractable Cu, Fe and Zn concentrations with depth reflects translocation of soluble sulphide weathering products down the profile from where sulphide oxidation (depletion) is predominantly occurring (0-300 mm). The contrasting

trend observed for 0.1M HCl extractable Pb concentrations is believed to reflect the immobility of PbSO₄ and the resulting higher concentrations of this sparingly soluble mineral near the surface of the tailings (Figure 10a).

Like Cu, Fe and Zn concentrations, total S and SO₄⁼ levels were similarly found to increase with depth (Figures 4.23 & 4.24). Total S levels were generally considerably higher than those of SO₄⁼ indicating that S is present predominantly as sulphides. Observed Fe and total S concentration trends at site 7 (characterised by a sharp increase in these elements below 200 mm depth) indicate that FeS₂ is by the far the most prevalent sulphide mineral in the Tui tailings.

A positive and significant correlation between pH and SO₄⁼ was identified at site 7 and 9. These parameters were used to identify what was postulated to be a zone of maximum sulphide oxidation between 200-300 mm depth where, very low pH values were found to coincide with maximum sulphate levels (Figures 4.26).

Characterisation of tailings samples obtained from 0-100 mm and 100-200 mm depths at the 12 grid sampling sites indicated that metal variability amongst the sites was high (Figures 4.18 to 4.21). Average Cu, Fe, Pb and Zn concentrations in the surface samples were approximately 70, 5200, 11900, 260 mg/kg respectively. Much greater concentrations were, however, identified at some sites. Total Pb concentrations, for example, were found to be in excess of 27,000 mg/kg at site 4 (Figure 4.21). Without exception average 'total' metal levels were higher in the subsurface tailings than the surface samples and tended to be much more variable. Average Cu, Fe, Pb and Zn concentrations in the 100-200 mm zone were approximately 140, 6800, 12400 and 500 mg/kg. With the exception of Fe and Pb, these concentrations were significantly higher than those found in the surface tailings.

0.1M HCl extractable Cu and Fe levels were similarly present at higher concentrations in the subsurface tailings. The average concentrations of 'labile' Cu and Fe in the surface tailings reached about 40 and 350 mg/kg respectively in the surface tailings and about 310 and 770 in the subsurface tailings (Figures 4.16 & 4.17). It is postulated that the differences (trends) observed between 'total' and 0.1M HCl extractable metal

concentrations in the surface and subsurface grid samples reflects that the surface tailings at the site have undergone more extensive oxidation than subsurface samples. Presumably the better aeration and warmer conditions prevailing in the surface samples have promoted biochemical oxidation of sulphide minerals within the surface tailings. With the exception of Pb, metals are postulated to have been extensively leached from the surface tailings as indicated by the generally significantly lower concentrations in which they are found in the surface 100 mm of the profile.

4.4 Acid Generation Potential

4.4.0 Introduction

The importance of assessing the net Acid Generating Potential (AGP) of sulphidic mine wastes is widely recognised, as this variable dictates the materials' plant growth characteristics and strongly influences mine site drainage quality (Chapter 3, section 3.4). Prior to this study very little was known about the extent and depth to which the Tui tailings had undergone oxidation and their potential to generate further acidity via oxidation. Considering that acid generation data is often used to estimate liming requirements of sulphidic material, knowledge about how the AGP of a material varies with depth has important implications for the incorporation of liming agents.

As discussed in Chapter 3 (section 3.4.1) there are several approaches to estimating the AGP of a material. Due to the perceived shortcomings of these traditional methods at estimating the AGP of polysulphidic materials, an alternative method was used to assess the AGP of the Tui tailings. The TAGP¹⁴ method is based largely on the acid-base accounting method described by Smith & Sobek (1978) and utilises the stoichiometry of pyrite and chalcopryrite oxidation outlined by Bruynesteyn & Hackl (1982). Although it was specifically designed to assess polysulphidic materials, containing two or more acid generating sulphide minerals, it is considered equally useful for determining the AGP of pyritic (monosulphidic) materials such as coal spoils.

This section describes the devised method and compares the results with those obtained from a distinctly different method of AGP assessment based on hydrogen peroxide

¹⁴ For the purposes of this study the devised AGP prediction method based on the tailings Cu and Fe content will be referred to as the TAGP (Theoretical Acid Generating Potential) method

oxidation (Miller *et al.*, 1994). The AGP_{HPO}^{15} method involved the use of hydrogen peroxide (H_2O_2) to rapidly oxidise remnant sulphides in the tailings. Following oxidation the AGP of the tailings was then estimated by back titrating the solution with a standardised base to calculate the amount of acid liberated during the reaction, per given quantity of material (Appendix 4(I)).

4.4.1 TAGP Method: Theory & Methodology

The TAGP prediction method is based on the principles used to assess the AGP of pyritic spoil in ABA¹⁶ (Chapter 3, section 3.4.1.1). The TAGP method is similar to ABA methods in that it uses stoichiometry to estimate the AGP of a given material. The TAGP method differs from traditional ABA methods in that:- (1) it enables the acid produced from non-pyritic sulphide minerals to be determined and (2) the material's AGP is estimated from sulphidic metal concentrations as opposed to sulphur concentrations.

The choice to base AGP estimates on metal concentrations rather than sulphur concentrations was made due to the occurrence of what were believed to be appreciable concentrations of galena (PbS) and sphalerite (ZnS) in the Tui Mine tailings. Although these sulphide minerals undergo oxidation, the reaction is not believed to liberate significant amounts of acid (Bruynesteyn & Hackl, 1982; Kwong, 1995). Literature review and preliminary characterisation of the Tui mine tailings (Chapter 4.2) indicate that pyrite (FeS_2) and chalcopryrite ($CuFeS_2$) are the two primary sources of acid in the Tui mine tailings. Thus, the determination of the sulphidic iron (Fe) and copper (Cu) content of the tailings enabled the relative concentrations of acid generating sulphide minerals to be determined. Sulphidic sulphur associated with the non-acidifying sulphides (galena and sphalerite) was effectively eliminated from the TAGP calculations.

The oxidative dissolution reactions of pyrite and chalcopryrite were used to stoichiometrically estimate an upper and lower TAGP value for the tailings (Bruynesteyn & Hackl, 1982).

¹⁵ The term AGP_{HPO} will, for the purposes of this study, be used to denote the Hydrogen Peroxide Oxidation Method of Miller *et al.*, 1984.

The upper limit (a worst case scenario) assumes that ferric iron (Fe^{3+}) completely hydrolyses to form ferrihydrite, whereas the lower limit assumes that all of the Fe is precipitated as hydronium-jarosite (Bruynesteyn & Hackl, 1982). The latter reaction liberates a comparatively low rate of acid (Table 4.19). If complete oxidation of the sulphide minerals occurs, the amount of acid produced in reality is likely to fall somewhere between the upper and lower limits (Chapter 3, section 3.3.2). Lime amendment rates, however, are often based on the upper limit as this provides the maximum potential oxidation (Bruynesteyn & Hackl, 1982).

The sulphidic Fe and Cu content of the tailings was estimated using two extractants; 0.1M HCl and 25% (v/v) HNO_3 . As discussed in chapter 4.2, one of the primary objectives borne in mind during the selection of these extractants was that they would not only satisfactorily estimate the AGP of the tailings but also provide useful information pertaining to the material's plant growth characteristics. The speed, safety and simplicity of the extractants and/or extraction procedures were also considered.

The Cu and Fe extracted by the 0.1M HCl was assumed to be non-sulphidic and therefore non-acid generating. The 'total' Cu and Fe content of the tailings was estimated using 25% HNO_3 . By assuming the majority of Fe and Cu in the tailing was present as pyrite, chalcopryrite and/or as occluded or soluble sulphate salts, it was postulated that the sulphidic Fe and Cu content of the tailings could be satisfactorily predicted as follows;

$$\text{Sulphidic Fe \& Cu} = \text{Fe \& Cu (25\% HNO}_3\text{)} - \text{Fe \& Cu (0.1M HCl)} \quad [\text{Equation 4.1}]$$

If it is assumed that Cu associates with the Fe and sulphur (S) in a ratio of 1:1:2 to form chalcopryrite (CuFeS_2), and that Fe associates with S in a ratio of 1:2 to form pyrite (FeS_2), the results obtained from equation (1) above can be used to stoichiometrically calculate the amount of pyrite and chalcopryrite in the tailings. The TAGP of the tailings was then estimated using the upper and lower stoichiometric values in Table 4.19.

¹⁶ ABA = Acid Base Accounting (see chapter 3, section 3.4.1.1 for further discussion).

Table 4.19 Acid potentially released from the oxidation of 1.0 mole of chalcopyrite and pyrite (Bruynesteyn & Hackl, 1982).

Sulphide	Lower Limit [moles H ₂ SO ₄]	Upper Limit [moles H ₂ SO ₄]
Pyrite	1.33	2.0
Chalcopyrite	0.33	1.0

To calculate the TAGP of the Tui mine tailings in this fashion several assumptions have to be made:- (1) It is assumed that the entire sulphidic Cu content of the tailings is present as ‘pure’ chalcopyrite and that based on empirical formula the Fe component of chalcopyrite is associated with Cu in a simple atomic weight ratio of 0.879:1.000 (ie. for every 1 g of Cu, 0.879 g of Fe is complexed in the chalcopyrite molecule). Therefore the pyritic Fe content of the tailings can be calculated as follows, Pyritic Fe = Fe[mg/kg] - (Cu[mg/kg] * 0.879). (2) The HNO₃ acid digestion does not render significant quantities of Fe and Cu associated with the silicate lattice layers soluble. ie. any Fe and Cu that is released from this phase is likely to be negligible. (3) The 0.1M HCl extracts predominantly Cu and Fe associated with sulphate.

The method for determining the sulphidic Fe and Cu content of the Tui Mine tailings is summarised below:-

- (1) The tailings samples were air-dried and sieved to < 2mm.
- (2) The non-sulphidic Cu and Fe content of the tailings was extracted using 0.1 M HCl as per the method outlined in Appendix 4(F).
- (3) Total Cu and Fe concentrations were extracted with 25% V/V nitric acid as per the method outlined in Appendix 4(E).
- (4) The sulphidic Cu and Fe content of the tailings was then estimated using Equation 4.1 above.

Appendix 4(H) includes working examples of the devised method for samples containing 1000 mg/kg Cu, 1000 mg/kg Fe, and a mixed sample containing 1000 mg/kg Cu and 10,000 mg/kg Fe as sulphides. The examples demonstrate how the sulphidic Fe and Cu concentrations are used to determine the acid generation potential of the tailings.

4.4.2 Acid Generating Potential Results

The TAGP of the tailings was assessed at each of the twelve sampling sites to enable the liming requirements of the surface 200 mm of the tailings profile to be ^{assessed} Analysis was conducted on two samples from each site obtained from 0 -100 mm and 100-200 mm depths (section 4.3.1.1).

TAGP results based on Cu and Fe metal analysis data presented in Figures 4.16-4.19, indicate that the TAGP of the surface tailings (0-100 mm) is less variable between sites and generally lower than that of tailings obtained from 100 to 200 mm depth (Table 4.20). Upper limit TAGP values (based on the complete hydrolysis of Fe³⁺), for example, were found to range from 12.2 to 30.7 Mg CaCO₃/1000 Mg of tailings in the surface tailings, where as the range in the 100 to 200 mm depth zone was far greater, varying from 3.6 to 79.6 Mg CaCO₃/1000 Mg of tailings.

Not all of the sites, however, were found to exhibit greater TAGP at depth. The surface tailings at sites 2, 6, 10 and 12 were found to exhibit higher TAGP values than the sub-surface tailings at the corresponding sites. This is postulated to reflect the occurrence of isolated layers of highly sulphidic tailings at or near the tailings surface as discussed in Chapter 4.2.2.

Table 4.20 AGP data [Mg CaCO₃/1000 Mg of tailings] based on the assessment of sites 1-12.
Presented data is based on 48 analyses conducted at sampling sites 1 to 12.

Depth [mm]	Average AGP Lower Limit	Average AGP Upper Limit	Range Lower Limit	Range Upper Limit
0-100	12.4 ± 3.2	18.7 ± 4.8	8.1 - 20.4	12.2 - 30.7
100-200	21.0 ± 15.0	31.8 ± 22.7	2.3 - 52.5	3.6 - 79.6

Spatial representation of the AGP values indicates that there are no obvious trends over the surface of the dam (Figure 4.28). This suggests that the prolonged saturation of the tailings at sites 1, 2, 8, and 11 has had little influence on the oxidation of acid generating sulphide minerals at these sites.

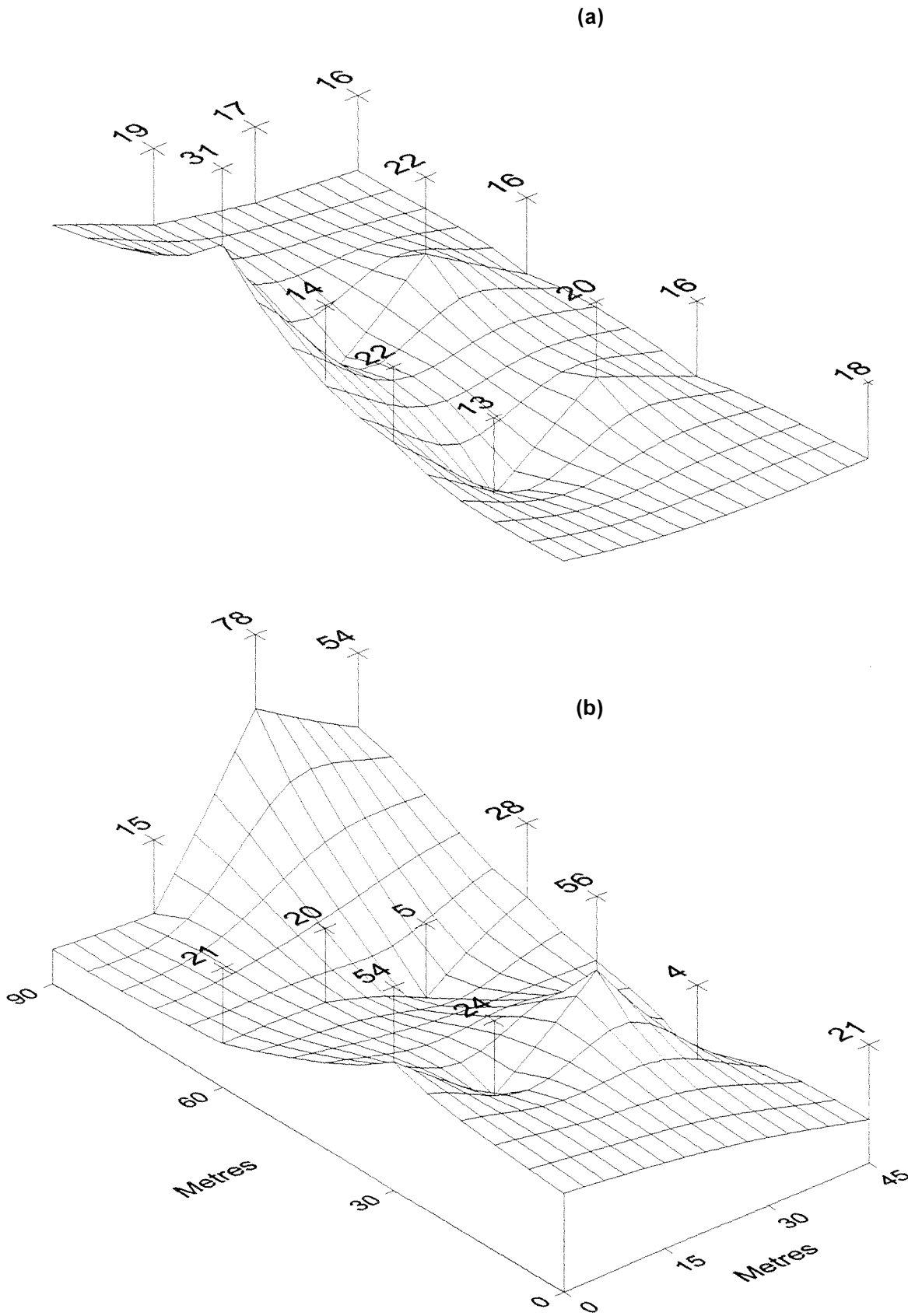


Figure 4.28 Tailings AGP [Mg CaCO₃/1000 Mg of tailings] in (a) 0-100 mm zone and (b) 100-200 mm zone
Assumes complete hydrolysis of ferric iron to ferrihydrite.

Table 4.20 indicates that complete oxidation of 1000 Mg of the surface tailings (0-100 mm) at the Tui mine site would liberate an amount of acid that would require between 12.4 and 18.7 Mg of CaCO_3 to neutralise it. Assuming a bulk density of 1.3 Mg/m^3 and a 100 mm liming depth, these rates are equivalent to 16.1 and 24.3 Mg CaCO_3 per hectare respectively. Similarly, neutralisation of the acidity potentially produced by the sub-surface tailings (100-200 mm) would require the addition of lime at a rate of between 27.3 and 41.3 Mg of CaCO_3 per hectare.

If the 'upper' and 'lower' limit values for each sampling depth are averaged and combined, an TAGP value of $20.1 \text{ MgCaCO}_3/1000 \text{ Mg}$ tailings is attained for the surface 200 mm of the tailings. Based on this value and neutralisation of the tailings to 200 mm depth, it is postulated that a lime application rate in the vicinity of 50 Mg/ha would prevent tailings re-acidification. Although very high by agricultural standards, liming rates such as these are commonly exceeded in mine reclamation schemes abroad (Dollhopf, 1992).

The relative contribution of pyrite and chalcopyrite to the Tui tailings' AGP was estimated from the concentrations of Fe and Cu respectively in the extractions. Pyrite was found to be by far the major contributor to the tailings' AGP, generally accounting for over 99% of the acidity potentially produced at each site (Table 4.21). Although as discussed in Chapter 3 (section 3.3.2) chalcopyrite releases comparatively lower rates of acid upon oxidation than pyrite, the primary reason for the much greater influence of pyrite on the TAGP of the tailings is due simply to its presence in far higher concentrations. Much of the Cu in the tailings was readily extracted with 0.1 M HCl and was thus deemed to be non-sulphidic and hence non-acid generating (Figure 4.11). Whilst the pyrite content of the tailings varied from 0.21% to as much as 4.71% in the upper 200mm of the profile, estimated chalcopyrite concentrations were generally far lower, ranging from less than 0.01% to about 0.2%.

Table 4.21 Average chalcopyrite and pyrite concentrations in the surface 200 mm of the Tui Mine tailings. [†] Refers to the percentage of the tailings TAGP attributable to pyrite oxidation. Presented data is based on 48 analyses conducted at sampling sites 1 to 12.

	Chalcopyrite [%]	Pyrite [%]	Pyrite[†] Contribution	Sulphide Ratio [Cu/Fe*100]
Average	0.04 ± 0.04	1.50 ± 1.04	99.11 ± 1.14	2.08 ± 2.77
Minimum	0.01	0.21	93.81	0.54
Maximum	0.20	4.71	99.76	15.02

Although the TAGP attributable to chalcopyrite was negligible at most grid sampling sites, results from site 2 suggest that about 6% of the potential acidity is ‘stored’ as chalcopyrite in the 100-200 mm sample. Samples from this site account for the high maximum sulphide ratio and large standard deviation for this parameter which was otherwise relatively constant from site to site (Table 4.21).

4.4.2.1 AGP of 100-mm Incremental Samples

To elucidate the results presented in sections 4.1.2.5 which indicated that the AGP of the Tui tailings increased with depth, the TAGP of the six-100 mm incremental samples obtained from site 7 was assessed. TAGP results based on Cu and Fe metal analyses presented in Figures 4.10 and 4.11 confirm that the TAGP of the tailings tends to increase with depth and indicate that an almost ten-fold increase occurs below 200 mm (Figure 4.29).

Estimates of the TAGP of the surface tailings’ (0-200mm) indicate that between 7.4 and 11.2 Mg CaCO₃/1000 Mg of tailings would be required to neutralise the acid potentially produced from the oxidation of pyrite and chalcopyrite within this zone. The composite sample (0-100 mm) obtained at grid sampling site 7 was found to exhibit comparable but slightly higher TAGP values (15.8 and 18.2 Mg CaCO₃/1000 Mg of tailings).

Due to the comparatively low concentrations of acid generating sulphide minerals in the surface tailings, the difference between the upper and lower TAGP limits appears relatively small (Figure 4.29). As the concentrations of pyrite and chalcopyrite increase with depth, however, the difference becomes more apparent. At 500-600 mm depth, for

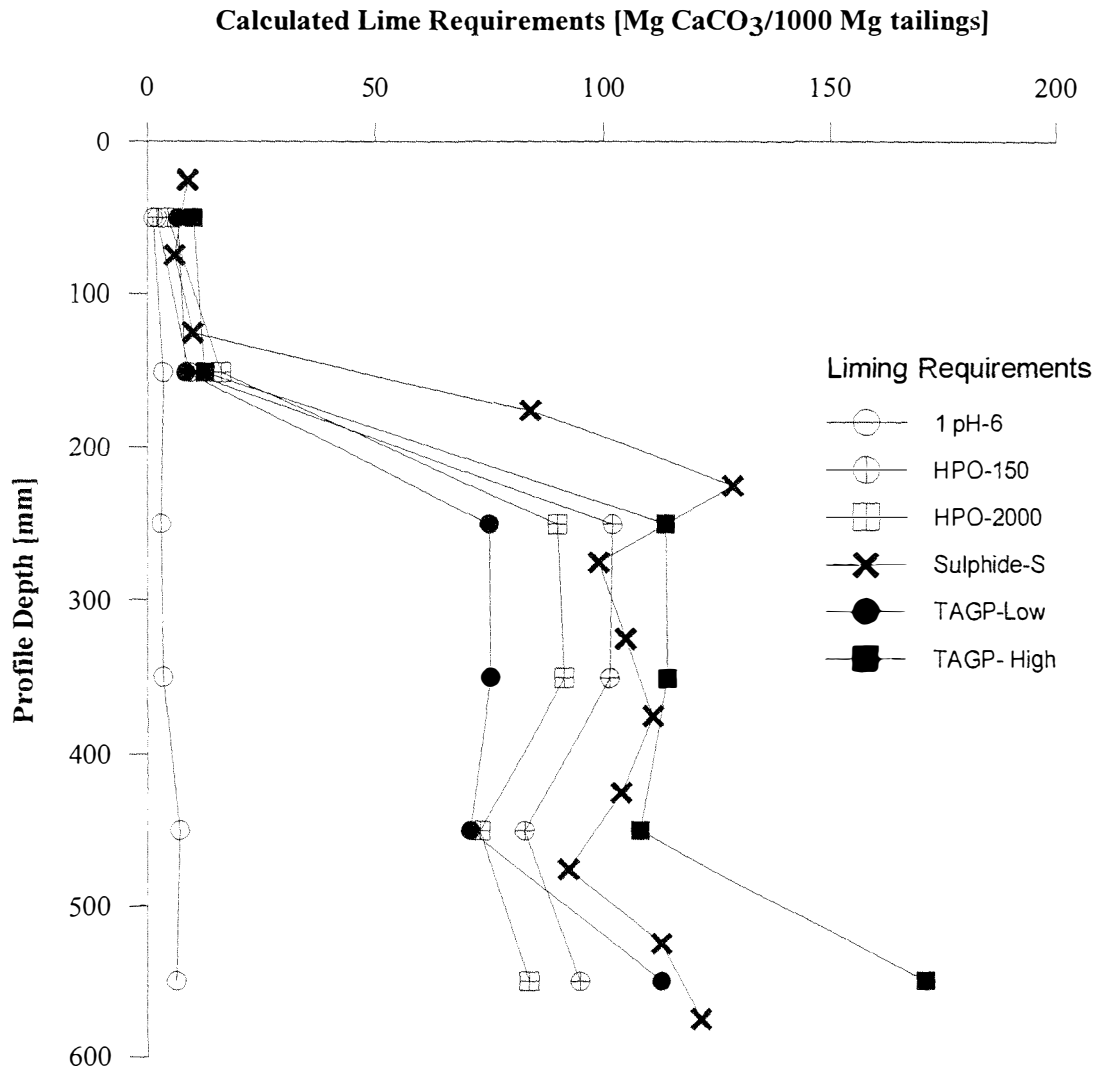


Figure 4.29 Liming requirements of the Tui tailings versus depth at site 7 as determined by: 48 hour pH buffering incubation (1 pH-6), hydrogen peroxide oxidation at 150 microns (HP-150) and 2000 microns (HP-2000), stoichiometry based on sulphur analysis (Sulphide-S) and Fe/Cu analysis (TAGP). Upper and lower limits for the latter method are specified by the suffixes 'High' and 'Low' respectively.

example the lower and upper AGP estimates differ by more than 58 Mg CaCO₃/1000 Mg of tailings. This difference is equivalent to about 75 Mg of CaCO₃ per hectare.

Analysis of the incremental samples indicates that between 98.5 and 99.5% of the potential acidity of the tailings is associated with pyrite. Chalcopyrite, in contrast is thought to contribute less than 2% of the ‘stored’ acidity of the tailings. Pyrite was found to constitute approximately 0.59% of the tailings in the upper 100 mm of the profile and about 10.13 % at 500-600 mm depth. At corresponding depths, chalcopyrite constituted just 0.02% and 0.38% of the tailings (Table 4.22).

Table 4.22 Sulphide content and metal ratios of tailings from Site 7
estimated from Fe and Cu extractions.

Depth [mm]	Chalcopyrite [%]	Pyrite [%]	Sulphide Ratio [Cu/Fe*100]
0-100	0.02	0.59	2.5
100-200	0.03	0.73	3.4
200-300	0.19	6.76	2.9
300-400	0.11	6.81	1.5
400-500	0.30	6.39	4.8
500-600	0.38	10.13	3.7

Although pyritic Cu and Fe concentrations were found to vary substantially with depth, the relative proportions of these minerals remained fairly constant at each of the sampling depths (Table 4.22). The sulphide ratios obtained from this site are similar to those obtained from the composite samples (Table 4.21), however, they contrast with results in Chapter 5 which suggest that sulphidic Cu has been preferentially leached from the surface tailings (0-200 mm).

To demonstrate the extent to which traditional soil liming requirement methods can severely underestimate the liming requirements of sulphidic material, included in Figure 4.29 are calcium carbonate equivalents for each of the incremental samples based on the pH buffering capacity of the tailings (Chapter 6.2). Whilst the amount of lime required to raise the pH of the tailings to 6.0 is seen to increase with depth, as the pH buffering capacity of the tailings improves, the increase is negligible in comparison to substantial

increase in the tailings TAGP (Figure 4.29). The tendency for pH buffering methods to grossly underestimate the liming requirement of sulphide bearing materials is further discussed in Chapter 6.

4.4.2.2 Comparison of AGP Results

For comparative purposes, the AGP of the six incremental samples were also assessed using two alternative methods; (1) sulphide sulphur analysis (Chapter 4.1) and (2) hydrogen peroxide oxidation (Miller *et al.*, 1994),

The AGP values stoichiometrically estimated from the sulphur data (as per the method outlined in Appendix 4(C)) were found to correlate well with the upper limit values of the TAGP method based on Fe and Cu content (Figure 4.29). Strong correlation between these two methods reflects the fact that pyrite is by far the most abundant sulphide mineral in the tailings and indicates that the AGP of the Tui tailings may have been adequately predicted by determining the sulphidic sulphur content of the tailings. The occurrence of non-acidifying sulphide minerals, galena and sphalerite in the tailings does not appear to have resulted in this method overestimating the AGP of the tailings as was predicted (Chapter 4.1).

The AGP_{H₂O₂} method of Miller *et al.* (1994) involved the addition of 15% hydrogen peroxide (H₂O₂) to rapidly oxidise the sulphide minerals in the tailings (Appendix 4(I)). The AGP of the tailings was then estimated by back titrating the solution with a standardised base to calculate the amount of acid liberated during the reaction per given quantity of tailings (see Appendix 4(J) for similar methodology). Initially, the AGP_{H₂O₂} method was found to produce comparatively low AGP values in all but the two uppermost samples (0-100 mm and 100-200 mm). More comparable values were attained for the sub-surface samples by increasing the H₂O₂ to tailings ratio. This was achieved by decreasing the tailings sample mass to 1.0g as suggested by Miller *et al.* (1994). A sample mass of 2.5 g was retained for the 0-100 mm and 100-200mm samples as the initial results indicated that the oxidising capacity of the H₂O₂ was sufficient to fully oxidise these samples which contained comparatively low concentrations of pyrite and chalcopyrite.

After modification of the H_2O_2 : tailings ratio, the results of the AGP_{HPO} method were also found to correlate well with those obtained from the TAGP method and confirmed that the tailings' AGP markedly increases below 200 mm depth (Figure 4.29). AGP_{HPO} values were generally found to lie between the upper and lower limits of the TAGP method. A notable difference was evident, however, in the 500-600 mm sample. At this depth the AGP_{HPO} values were found to be much lower than those obtained from the TAGP method (Figure 4.29). Whilst a number of factors are known to influence the analytical results obtained from AGP procedures based on H_2O_2 oxidation (Finkelman & Giffin, 1986), it was considered beyond the scope of this study to isolate the exact cause of the disparity between the two methods. A noticeable increase in the sulphidic sulphur content of the tailings (Figure 4.29), however, indicates that the AGP_{HPO} method is likely to have underestimated the AGP of the 500-600 mm sample due presumably to the exhaustion of added H_2O_2 resulting in incomplete oxidation of pyrite and chalcopyrite.

The grain size of the samples was also found to affect the AGP of the tailings when assessed using the AGP_{HPO} method. Grinding the tailings to $< 150 \mu\text{m}$ was found to appreciably increase the AGP of 4 of the 6 incremental samples (Figure 4.29). No significant difference, however, was noted in the sulphide-depleted surface samples (0-100 and 100-200 mm samples). These results are consistent with findings of previous studies which have identified surface area (grain size) as one of the dominant factors effecting pyrite reactivity with hydrogen peroxide (O'Shay *et al.*, 1990; Finkelman & Giffin, 1986).

In contrast to the AGP_{HPO} method, the grain size of the tailings was not found to influence the AGP of the tailings when estimated using the method based on metal content (TAGP method). This result is readily explained by the comparatively severe nature of 25% HNO_3 and its ability to more effectively oxidise pyrite and chalcopyrite.

4.4.3 Neutralisation Potential

The Neutralisation Potential (NP) of a material is defined as the ability of a material to neutralise strong acid (Sengupta, 1993). The inherent neutralisation potential of a material is related primarily to the amounts of alkaline carbonates, exchangeable bases,

and weatherable silicates that it contains. The most effective minerals for neutralising acid are the carbonate minerals such as calcite (CaCO_3), magnesite (MgCO_3), and dolomite ($\text{CaMg}(\text{CO}_3)_2$) (Lapakko, 1994). Calcite, however, is usually by far the greatest contributor to the NP of mine wastes due to its common occurrence, relatively high rate of reaction and high neutralising capacity (Dent, 1986).

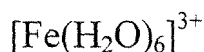
The most commonly used methods to assess the NP of mine wastes are static procedures which involve reacting a sample with a known amount of standardised acid, heating the solution to assure complete dissolution of the bases and back-titrating with a standard base (Sobek *et al.*, 1987). Although several variations exist (Smith *et al.*, 1974; Sobek *et al.*, 1978; Ritcey, 1989) most of these procedures are based largely on the method of Jackson (1958) which was initially designed to assess the neutralising potential of agricultural limestone (Costigan *et al.*, 1981). The method involves heating the sample in an acid solution to ensure complete dissolution of the bases which allows the maximum neutralisation potential to be measured including that contributed by silicates and dolomite (Sobek *et al.*, 1987). Calculation of the proportion of added acid that has been neutralised by the sample's base components allows for the ready conversion to CaCO_3 equivalents. The NP of a material is then combined with its AGP to estimate its NAGP (Net Acid Generating Potential).

4.4.3.1 Neutralising Potential Assessment

Due to the very low pH of the tailings, the high quartz component and absence of significant quantities of Ca (Table 4.2), the neutralising potential of the various Tui tailings samples was expected to be extremely low. Although small quantities of the clay mineral kaolinite were detected in the tailings by XRD analyses (Chapter 5), this mineral has low ion-exchange capacity and therefore a low ability to buffer pH change.

An initial assessment of the neutralising potential of the tailings was conducted by reacting 1.0g of tailings with 50 mL of standardised 0.10M HCl at 80 °C for approximately ½ an hour. The solution was allowed to cool and the excess acid was then titrated to the end point of phenolphthalein (pH = 8.3) using a standardised 0.10M NaOH solution. pH 8.3 was used to ensure that all the Fe^{2+} produced from neutralisation by siderite (if present) would be oxidised to Fe^{3+} (Costigan *et al.*, 1981).

Problems arose with this method due to the formation of ferric and ferrous hydroxides which masked the end-point colour change. At low pH values ($\text{pH} \leq 2.3$) ferric ion (Fe^{3+}) is stable and remains in solution coordinated with 6 water molecules as the following complex;



It was found as the pH of the solution was raised much above pH 2.5, by the addition NaOH, colloidal gels began to precipitate out of solution. Ferric iron is renowned for its tendency to hydrolyse and/or form complexes and even at pH values of about 2.5 - 3.0 the extent of hydrolysis is substantial (Cotton & Wilkinson, 1972). The binuclear species shown in Figure 4.30 is thought to form at these relatively low pH values, however, at higher pH more highly condensed species are formed resulting in the precipitation of colloidal gels and ultimately hydrous ferrous oxides ($\text{Fe}(\text{OH})_3$).

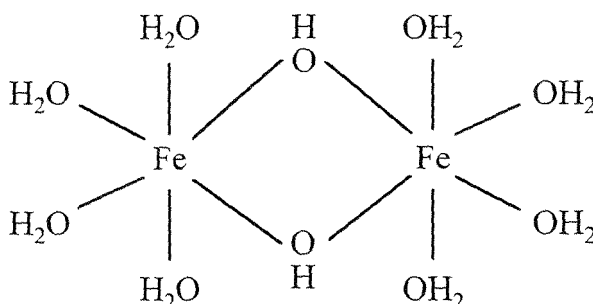
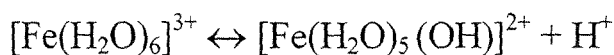


Figure 4.30 Binuclear Fe complex (source Cotton & Wilkinson, 1972)

As the Fe^{3+} complex is hydrolysed, hydrogen ions are released into solution which act to buffer pH change as they react with the NaOH titrate.



The precipitation of Fe^{3+} and the subsequent liberation of H^+ is an integral reaction in the overall process of acid mine drainage (Sengupta, 1993). The colour change of phenolphthalein from colourless to pink proved impossible to detect due to the large amount of iron hydroxides present in the solution at pH values in the range of the

titration endpoint (8.3). Thus, the formation of the iron hydroxide was not only found to hinder the visual detection of the end-point but also tended to buffer pH change by liberating H⁺ into solution. Whilst the overall effect of this buffering reaction may be negligible if Fe³⁺ or Fe²⁺ concentrations are low, the effect of the reaction may result in an underestimation of the samples neutralising potential if high concentrations of these ions are present in solution.

To avoid the problem of the endpoint of the titration being obscured by colloidal precipitates the method of Sobek *et al.* (1978) was alternatively used to assess the NP of the Tui Mine tailings. An endpoint of 7.0 was used and attained using a pH meter as opposed to an indicator (Appendix 4(J)). The lower endpoint pH and use of pH meter allowed the endpoint of the reaction to be accurately assessed and was postulated to decrease the effects of the buffering action of the iron hydroxide complexes.

Both HCl and water titrations were performed in triplicate, and the volume results were averaged and converted to molar units.

4.4.3.2 Neutralising Potential Results

The NP of two incremental samples from site 7 were assessed (0-100 and 500-600 mm) using the method outlined in Appendix 4(J). Both samples gave slightly negative neutralising potential results indicating that the NP of the tailings samples was negligible and that the samples were liberating small amounts of acid during the reaction.

Table 4.23 Neutralising Potential of sampling site 7 tailings.
The results are the averages of 4 replicate analyses conducted on each sample.

Sample Depth [mm]	Moles of HCl initially added	Moles of NaOH consumed by HCl sample	Moles of NaOH consumed by blank	Neutralising Potential [Mg CaCO ₃ / 1000 Mg]
0-100	4.97 x 10 ⁻³	5.135 x 10 ⁻³	7.0 x 10 ⁻⁵	-2.38
500-600	4.97 x 10 ⁻³	5.244 x 10 ⁻³	1.68 x 10 ⁻⁴	-2.65

The negative NP results are postulated to have occurred as a result of H^+ liberation due to the hydrolysis of Fe^{3+} and Fe^{2+} complexes as previously discussed. The titration of the tailings samples involved raising the pH of the solution to 7.0. This value exceeds the initial pH of the tailings and is sufficiently high to cause mass precipitation of colloidal gels.

Whilst clearly erroneous results were obtained using the NP titration method of Sobek *et al.* (1978), the results confirmed that the Tui tailings samples have negligible ability to neutralise acid produced from the oxidation of sulphide minerals. The inability of the tailings to neutralise significant amounts of liberated acid stems from the fact that they contain negligible quantities of alkaline carbonates, organic matter, exchangeable bases and high CEC clays. Because the Tui mine tailings have negligible NP the net acid generating potential of the Tui tailings can be adequately estimated from the materials' ability to produce acid.

4.4.4 Conclusions on AGP Characterisation

Analyses of incremental tailings samples at site 7 indicates that the AGP of the tailing dramatically increases below 200mm depth (Figure 4.29). Whilst predicted TAGP values were not considered to be particularly high within the surface 200 mm of the profile at this site, very high TAGP values ($> 100 \text{ Mg CaCO}_3/1000 \text{ Mg of tailings}$) were encountered in the subsurface tailings. Predicted AGP results obtained using the hydrogen peroxide method of Miller *et al.*, (1994) and sulphur analysis were found to agree very well with stoichiometrically estimated values obtained from Fe and Cu data (TAGP values) and confirm that the Tui tailings have considerable potential to generate acidity below 200 mm depth.

In accordance with site 7 data, TAGP values in the grid samples (sites 1 to 12) were generally found to increase with depth (Figure 4.28). By averaging the upper and lower TAGP values over the 200 mm depth an average TAGP value of about $20 \text{ Mg CaCO}_3/1000 \text{ Mg of tailings}$ was obtained. Using a tailings bulk density value of 1.3 Mg/m^3 and a liming depth of 200 mm this equates to a liming rate of about 50 Mg per hectare. Incorporation of this rate of lime into the surface 200 mm of the tailings should

in theory be sufficient to prevent long term reacidification of the tailings by neutralising acid generated by pyrite and chalcopyrite oxidation.

Based on Fe stoichiometry it was estimated that the pyrite content of the surface tailings (0-200 mm) ranges from about 0.2% to 4.7%. Chalcopyrite concentrations in the tailing were estimated to be comparably much lower (0.01% to 2%). These estimates indicate that pyrite is by far the primary source of potential acidity in the Tui tailings. The very high proportion of pyrite in the tailings explains the close approximation of upper limit TAGP values using predicted sulphide S data (Figure 4.29).

Estimation of the Tui tailings Neutralising Potential (NP) based on methods commonly used to estimate the NP of colliery spoil proved problematic due to the precipitation of Fe^{2+} and Fe^{3+} hydroxide complexes and concomitant liberation of H^+ during Fe hydrolysis. The results, however, combined with XRD analysis (Chapter 5) and ICP-AES analysis confirmed that the NP of the Tui tailings is negligible and need not be incorporated in net AGP calculations.

The TAGP method based upon Cu and Fe stoichiometry proved to be a useful and rapid method to characterise the Tui tailings. Not only did the method provide a useful indication of the materials ability to produce acidity but also yielded important information about the quantities and potential availability of Cu and Fe in the tailings. In this respect the TAGP method is clearly superior to those methods based on sulphur analysis or hydrogen peroxide oxidation.

4.5 Chapter 4 Summary & Conclusions

- Characterisation of the Tui mine tailings indicates that they do not exhibit any obvious physical traits likely to severely inhibit the establishment of vegetation. The surface tailings (0-200 mm) with their moderate bulk density, low to moderate resistance to penetration and predominantly fine sand to silt-sized texture are considered to be an adequate rooting medium. The upward migration of contaminated pore water (via capillary rise) and the presence of a very high water table at the eastern end of the dam are, however, potential problems that may hinder the establishment of plants should attempts be made to revegetate the tailings without

the emplacement of capping materials. The tailings' lack of cohesion may similarly hinder attempts to revegetate the site. Surface erosion may damage, upheave or even bury emergent seedlings during severe wind or rain storms.

- In terms of their chemical characteristics the Tui tailings are considered to be an extremely hostile and chemically variable potential plant growth medium. ICP-AES and FAAS analysis indicates that they contain elevated concentrations of several potentially phytotoxic elements. At several sampling sites, for example, Pb was found to constitute more than 2% of the tailings by weight. Whilst acidic conditions and very high Pb concentrations prevail in the surface tailings at most sites, they contain comparably low concentrations of most other heavy metal elements. Likewise the AGP of the surface tailings as determined by static tests was relatively low.
- Characterisation of subsurface tailings (>200 mm depth) in contrast, indicated that they contain very high concentrations of metals primarily as sulphides and have a very high capacity to generate acidity via sulphide oxidation. The large increase in AGP below 200 mm indicates that the tailings below this depth may be largely unoxidised and capable generating large volumes of AMD in the environmental conditions prevailing at the site unless remedial steps are taken to reclaim the site. The disturbance and exposure of unoxidised tailings at the site must be avoided to minimise the likelihood of exacerbating sulphide oxidation at the site and AMD.
- Based on the results of chemical characterisation it is postulated that the surface tailings (0-200 mm) have undergone extensive oxidation and leaching which has substantially decreased the concentrations of most metals.
- In terms of the potential of the tailings to host vegetation the results clearly indicate that the surface tailings are most suited to plant growth providing extreme acidity and nutrients imbalances are addressed and Pb remains in a form that is highly insoluble and thus largely unavailable to plants.
- The surface tailings are considered to be relatively inert in terms of their AGP, although it is estimated that a liming rate of approximately 50 Mg per hectare would be required to prevent the long term reacidification of the tailings resulting from sulphide oxidation.

Chapter 5

Mineralogical Analysis & Scanning Electron Microscopy

5.0 Introduction

This chapter further characterises the Tui mine tailings in terms of their mineralogy using X-ray Diffraction Analysis (XRD) and Energy Dispersive X-ray Spectrometry (EDS). In addition, Scanning Electron Microscopy (SEM) is used to investigate the variation in mineral surface morphology with horizon depth to establish if chemical trends observed in Chapter 4 have been manifested physically.

5.1 X-ray Diffraction Analysis

The technique of XRD mineral identification is based on principle that each crystalline substance has a characteristic arrangement of atoms which diffract X-rays in a unique and hence characteristic pattern (Whitton & Churchman, 1987). Although XRD analyses has been used to investigate the mineralogy of ore materials, andesitic rocks and stream sediments associated with the Tui Mine (Cochrane, 1969; Wodzicki & Weissberg, 1970; Tay, 1980), there appears to have been very little analysis carried out on the tailings material *per se*. Whilst Pang (1992) mentions the identification of quartz, pyrite, some sphalerite and kaolinite and a “*little*” feldspar in a bulk sample of the Tui mine tailings using XRD, the author stops short of discussing the relative proportions of the minerals and the source of the data.

Cochrane (1969) used XRD to determine the purity of sphalerite and the presence of “*well-crystallised kaolinite*” in the Tui ore. Wodzicki & Weissberg (1970) similarly used XRD to identify, quartz, chlorite, illite and inter-layered illite-montmorillonite in a study investigating the alteration and origin of sulphide mineralisation at the Tui Mine. Although Tay (1980) did not conduct XRD analyses on the Tui tailings *per se*, analysis of sediments derived from Tui mine adits and the Tui and Tunakohoa Streams was undertaken. In Tay’s study, quartz galena, sphalerite and cerussite were identified in No. 7 adit sediments. The XRD traces of Tui Stream sediments (taken from below the confluence of the tailings dam

stream), however, did not indicate the presence of sulphide minerals despite the high concentrations of Cu, Cd, Fe, Pb and Zn in the sediments. Iron was therefore postulated to be predominantly in the form of ferric oxy-hydroxides which are amorphous to X-rays and have a tendency to 'scavenge' and adsorb heavy metals such as Cu, Cd, Pb and Zn. Heavy liquid (tetrabromoethane) separation of sediments from the Tunakohoa Stream conducted by Tay (1980) facilitated the identification of sphalerite and pyrite in the sediments. An attempt by Tay to quantify pyrite concentrations by relative peak intensity failed, however, due to complications relating to the overlapping peaks of sphalerite and pyrite at 1.63, 1.91 and 3.12 Å. Tay (1980) concluded that based on XRD analysis of the sediments, peak intensity values did not satisfactorily predict pyrite content.

5.1.1 Aims of X-ray Diffraction Study

Analytical data reported in Chapter 4 indicates that Cu, Fe and Zn are present in relatively low concentrations in the top 200 mm of the tailings profile. The distribution of Pb, in contrast, was found to be relatively uniform with depth. It was postulated that the oxidation of sulphide minerals and the subsequent dissolution and leaching of weathering products into the aquatic environment has lead to the specific depletion of some metals (Table 5.1). Sulphur analyses and pH data from the profile samples support this theory. Thus the primary aims of the XRD analyses reported in this chapter was to:-

- (1) Identify the different mineral phases in the tailings within the surface 600 mm of the profile.
- (2) Confirm observed trends from previous analytical work that indicates that concentrations of sulphides increase with depth.
- (3) To ascertain if and why Pb appears to be resistant to leaching from the surface tailings (0-200 mm).

5.1.2 Preliminary X-ray Diffraction Method

The samples used for this study correspond to those described in Chapter 4 (section 4.3.1.2) and were obtained from an open pit excavated near the centre of the tailings at the western end of the dam (grid sampling site 7). Six, 100 mm incremental samples were collected at

this site to a depth of 600 mm. The samples were air-dried, ground to $<150\ \mu\text{m}$ with an agate mortar and pestle and prepared for XRD analysis by packing holders with non-oriented powder samples. A sample ore from the Tui Mine was similarly prepared.

Analysis of the samples was undertaken using a Phillip's PW 1729 X-ray Generator and a PW 1840 Diffractometer, operating at 40 kV and 40 mA. A cobalt anode was used and the samples were run from 2° to 75° (2θ). Sietronics XRD trace processing software (Version 1.0) was used to analyse the traces and to identify the mineral phases present in the tailings samples.

5.1.3 Preliminary X-ray Diffraction Results

Results of the XRD analyses indicated that the tailings were predominantly quartz, with minor kaolinite (Figure 5.1a). Samples below 200 mm were shown to contain small quantities of pyrite. This trend is consistent with FAAS¹ data which show an almost tenfold increase in total Fe content below the 200 mm depth (Table 5.1). The XRD trace indicated that the 0-100 mm sample contained no detectable pyrite (Figure 5.1a), whereas the 500-600 mm sample was shown to contain a small but significant amount of pyrite as indicated by the presence of an additional 7 peaks associated with this mineral (Figure 5.1b).

The Tui ore sample analysed was found to consist primarily of quartz, galena, sphalerite and chalcopyrite. The presence of kaolinite or pyrite in the ore were not detected. It is postulated that the presence of pyrite was masked by sphalerite which, as previously mentioned, has similar major d-spacings to pyrite. FAAS data indicates that the sample contained over 4 times as much Zn as Fe (Table 5.1). The presence of relatively high proportions of sphalerite in the Tui ore is consistent with the findings of previous mineralogical studies reported in Chapter 2 (section 2.6).

¹ Flame Atomic Absorption Spectrometry

5.2 Sodium Polytungstate Separation

Inspection of the XRD traces indicated that the various tailings samples were dominated by quartz which effectively diluted the heavy mineral fraction (HMF) of the tailings. To mitigate this problem density separation was used to isolate the HMF of the tailings from the light mineral fraction (LMF). This was achieved using a solution of sodium polytungstate (SPT) with a bulk density (ρ_b) of approximately 2.8 g/cm³ (Callahan, 1987). Thus for the purposes of this study the LMF is defined as the fraction of the tailings made up of particles with a ρ_b of less than 2.8 g/cm³. Conversely, the HMF is defined as the fraction of tailings composed of particles with a ρ_b of greater than 2.8 g/cm³.

Table 5.1 Total elemental concentrations of selected metals and minerals detected by XRD in unseparated Tui mine tailings. The minerals are listed in alphabetical order and abbreviated as follows:
ch = chalcopyrite (CuFeS₂); gn = galena (PbS); ka = kaolinite (Al₂Si₂O₅(OH)₄);
py = pyrite (FeS₂); qtz = quartz (SiO₂); sl = sphalerite (ZnS).

Sample	Depth [mm]	Minerals Detected	Fe [ppm]	Cu [ppm]	Pb [ppm]	Zn [ppm]
1	0-100	ka, qtz	2967	75	7538	347
2	100-200	ka, qtz	3660	113	10568	486
3	200-300	ka, py, qtz	32443	746	11590	1885
4	300-400	ka, py, qtz	32892	1465	5857	1893
5	400-500	ka, py, qtz	32475	2185	5060	5462
6	500-600	ka, py, qtz	49877	1961	4058	4388
Tui ore	NA	ch, gn, qtz, sl	43279	10169	186486	185266

5.2.1 Sodium Polytungstate Separation Method

Half gram (0.500g) tailings samples were placed in centrifuge tubes with narrow stems. Approximately 5 mL of SPT was added to each tube and the solutions were stirred gently to disperse the grains and break up aggregates. The tubes were then centrifuged for 5 minutes at approximately 1500 rpm. The LMF of the samples were decanted from the test-tubes into funnels containing filter paper (MFS, No. 1). This was achieved by creating a seal at the narrow section of the stem containing the HMF, with a glass rod. The tubes were rinsed to ensure that any of the tailings LMF adhering to the walls of the tubes was removed. The samples were rinsed thoroughly with deionised water to remove the SPT and then placed in

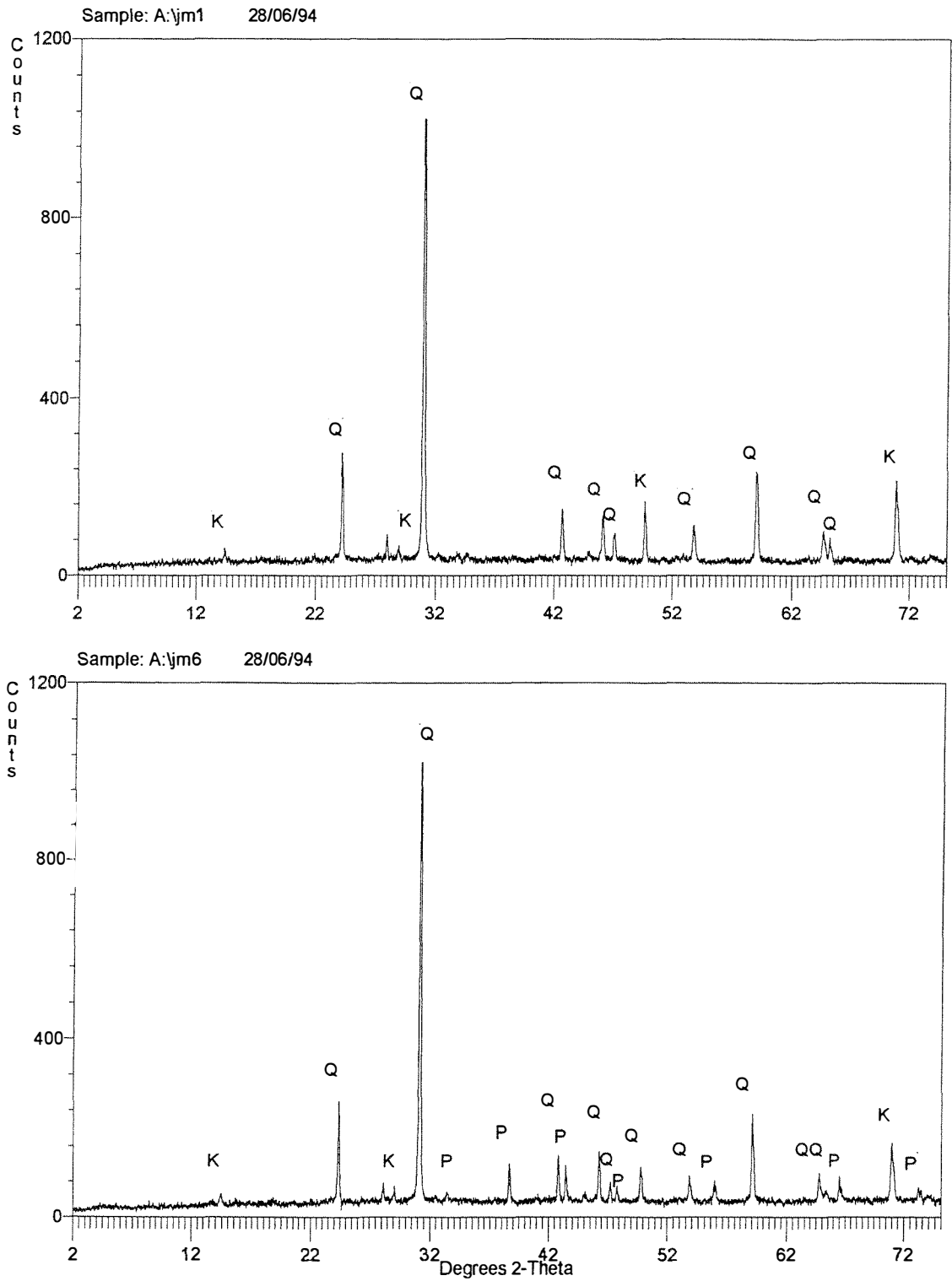


Figure 5.1 (a) XRD trace of 0-100 mm tailings sample and **(b)** XRD trace of 500-600 mm tailings sample containing detectable pyrite (P) as well as kaolinite (K) and quartz (Q).

an oven at 105 °C and left to dry over night on filter papers (Whitton & Churchman, 1987). Following the removal of the LMF, the HMF was rinsed from the bottom of the centrifuge tubes with distilled water and similarly collected and dried. Both fractions of each sample were then weighed to 4 decimal places to enable the relative proportions of each fraction to be calculated (Table 5.2).

5.2.2 X-ray Diffraction Method

Due to the greater number of samples a Phillip's 4-kVa PW 1710 instrument with a PW 1050/80 goniometer operating at 40 kV and 60 mA was used in conjunction with a 42 sample changer system (a PW 1775 unit). A broad-focus cobalt anode tube was used and the samples were scanned from 2° to 90° 2 θ .

The tailings and ore samples were run as acetone slurry mounts which were prepared by mixing ground tailings with a few drops of acetone on a glass slide before evenly distributing the slurry over the whole slide and allowing it to air-dry (Whitton & Churchman, 1987).

5.2.3 Sodium Polytungstate Separation Results

Density separation of the tailings enabled a semi-quantitative estimate of the relative proportions of heavy to light minerals in the mine tailings to be made and provided useful insight into the probable distribution of sulphide minerals within the profile. Results from the SPT density separation of the tailings indicate that the HMF generally increases with depth. The HMF was found to increase from approximately 1.5% in the surface sample (0-100mm) to over 16% in the bottom sample (500-600 mm) (Figure 5.2).

Figure 5.2 indicates that there is a substantial increase in the HMF of the tailings below 200 mm depth. XRD analysis of the LMF also indicates a distinct change in the composition of the tailings below 200 mm where pyrite and/or sphalerite is detected (Table 5.2). The increase in heavy minerals with depth is consistent with FAAS analyses which shows a corresponding increase in the concentrations of Cu, Fe and Zn with depth (Table 5.1) and

correlates well with AGP values presented in Figure 4.29. The non-depletion of Pb from the upper profile is readily explained by the detection of anglesite (PbSO₄) in the HMF of the tailings².

Table 5.2 Heavy mineral fraction (HMF) and XRD identified minerals. Minerals are listed alphabetically and abbreviated as follows: an-anglesite (PbSO₄); ca-calcite (CaCO₃); ch-chalcopyrite (CuFeS₂); gn-galena (PbS); ka-kaolinite (Al₂Si₂O₅(OH)₄); qtz- quartz (SiO₂); sl/py- sphalerite (ZnS) and pyrite (FeS₂).

Sample	Depth [mm]	HMF [%]	LMF Minerals Detected	HMF Minerals Detected
1	0-100	1.45	ka, qtz	an, gn, ka, qtz, sl/py
2	100-200	1.55	ka, qtz	an, gn, ka, qtz, sl/py
3	200-300	7.23	ka, qtz, sl/py	an, ch, gn, ka, qtz, sl/py
4	300-400	8.11	ka, qtz, sl/py	an, ch, ka, qtz, sl/py,
5	400-500	9.85	ka, qtz, sl/py	an, ch, gn, ka, qtz, sl/py
6	500-600	16.25	ka, qtz, sl/py	an, ch, gn, ka, qtz, sl/py
Tui ore	NA	77.7	gn, ka, qtz, sl/py	ca, ch, gn, ka, qtz, sl/py,

The presence of pyrite and/or sphalerite in LMF indicates that SPT density separation was not 100% efficient at separating the quartz and kaolinite from the sulphide minerals. Pyrite and sphalerite have specific gravities of approximately 5.0 and 4.1 g/cm³ respectively (Deer *et al.*, 1992) and are therefore far denser than the SPT solution used. Contamination of the LMF with these minerals, in particular pyrite, was unexpected and explained only after examination of the sample grains under an optical microscope (transmitted light).

Temporary mounts of the tailings were made for examination by sprinkling a small quantity of the material on an optical slide and adding two or three drops of clove oil and a cover slip (Whitton & Churchman, 1987). Examination of the LMF grains at 10 x magnification showed a significant portion of the quartz grains contained inclusions of opaque material, presumably pyrite and/or sphalerite. The sulphide inclusions were sufficiently small to prevent the overall density of the particle to rise above 2.8 g/cm³, thus providing a mechanism for the ‘contamination’ of the LMF with detectable concentrations of sulphide minerals. The intrinsic association of the quartz and pyrite also explains the presence of a

² See further discussion in section 5.2.4.

significant amount of quartz in the HMF of the tailings. Due to the comparatively high density of the heavy minerals, a relatively large amount of quartz was carried through into the HMF fraction of the tailings by the sodium polytungstate solution. The efficacy of this method at separating the mineral fractions of the tailings is therefore dependant on the sample containing discreet mineral grains and could theoretically be improved by finer grinding of the tailings prior to separation. Excessive grinding, however, is undesirable as it reduces the quality of the XRD patterns generated by mineral samples.

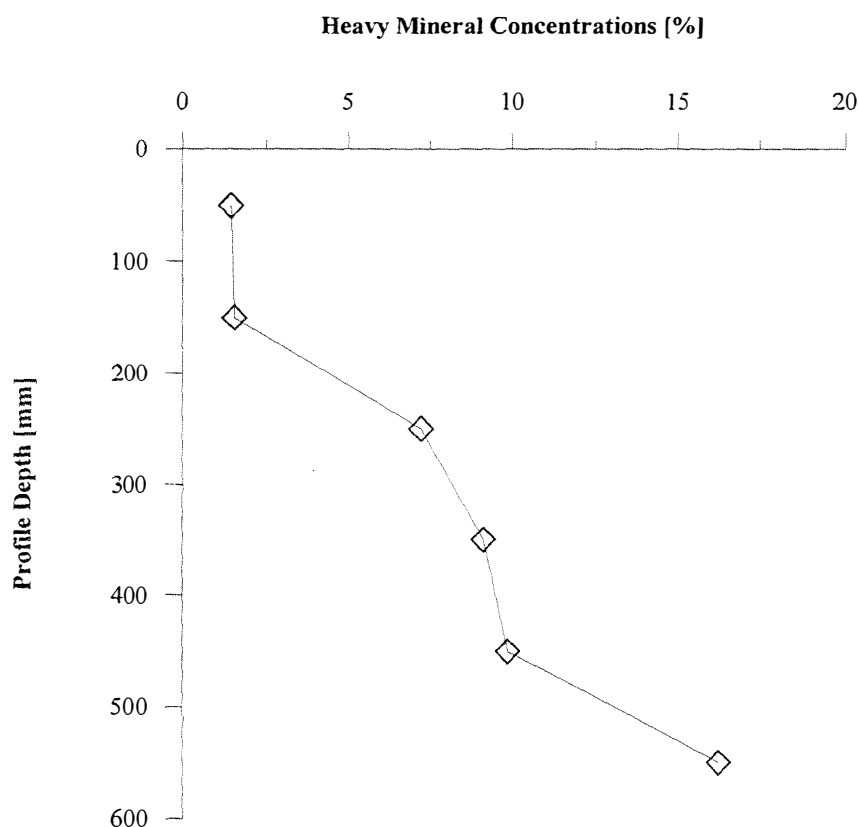


Figure 5.2 Heavy mineral contents versus depth in incremental samples.

5.2.4 X-ray Diffraction Results

XRD analyses of the heavy mineral fraction (HMF) of the Tui mine tailings identified an additional 4 minerals that were not detected in the non-separated tailings samples. These

included anglesite, chalcopyrite, galena and sphalerite. An increase in the relative abundance of pyrite and/or sphalerite with depth was indicated by a significant increase in the intensity of peaks corresponding to these minerals. No attempt, however, was made to quantify the relative proportions of the individual minerals as comprehensive FAAS analyses of the tailings provided an adequate indication of the approximate proportions of minerals in the various samples (Table 5.1).

Interpretation of the XRD patterns indicates that anglesite (PbSO_4) is the most prevalent Pb mineral in the top 300 mm of the profile. Although anglesite has been identified in Tui ore samples in several studies (Courtney *et al.*, 1990), its limited occurrence in the ore indicates that the origin of this mineral in the tailing is primarily from *in situ* weathering of galena. The identification of anglesite confirms that the surface tailings are actively oxidising.

The relatively high concentrations of Pb in the upper profile of the Tui mine tailings compared to Cu, Fe and Zn is fully explained by the extremely low solubility and high stability of anglesite (Table 5.3). Under oxidising conditions anglesite (PbSO_4) is stable between pH values of about 0.4 and 5 (Brookins, 1988). Comparable weathering products of sphalerite, pyrite and chalcopyrite are generally highly soluble under similar pH conditions (Table 5.3) and are likely to have been leached from the upper profile by infiltrating rain and surface water. The relative depletion of Cu, Fe and Zn from the upper profile and immobility of Pb is therefore largely a function of the stability/solubility of the various weathering products of the remnant sulphide minerals within the tailings.

Table 5.3 Solubility and density of selected sulphate minerals (Aylward & Findlay, 1974).

Compound	Name	Solubility [g/100g]	Specific gravity [g cm ⁻³]
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Chalcanthite	22	2.3
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Melanterite	29.5	1.9
PbSO_4	Anglesite	0.0045	6.4
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	Goslarite	58	2.0

The water quality studies of Tay (1981) and Pang (1992) confirm that substantial amounts of Cu, Fe, Zn and other elements are currently being leached into surface and ground water at the Tui mine site. The relative immobility of Pb is reflected by the fact that Fe and Cu concentrations in leachates emanating from the tailings dam tend to be at least two orders of magnitude greater than Pb concentrations (Table 2.1).

Density separation of the Tui ore using SPT facilitated the identification of kaolinite and pyrite in the LMF and HMF respectively. XRD analysis of the ore sample also indicated the presence of calcite in the HMF sample. Calcite is a common gangue mineral associated with hydrothermal sulphide deposits and has been identified in several previous mineralogical studies of the Tui ore (Courtney *et al.*, 1990). The fact that calcite was not detected in the LMF of the ore material is surprising given that due to its relatively low specific gravity (2.7 g/cm^3) it should have been separated into this fraction rather than the HMF. XRD analysis of the tailings does, however, clearly indicate that calcite was not a major constituent of the Tui ore sample.

The absence of XRD-detectable calcite in the tailings was not surprising considering the extremely acidic conditions which prevail at most depths. Most calcite initially deposited as gangue derived from the processing of ore has undoubtedly reacted with hydrogen ions produced by the oxidation of pyrite and chalcopryrite in the tailings, resulting in its depletion from at least the upper 600 mm of the tailings profile.

5.3 Scanning Electron Microscopy & Energy Dispersive X-ray Spectrometry

Scanning Electron Microscopy (SEM) has emerged as a powerful tool for examination of material surfaces. It is particularly useful for producing images of the surface textures of mineral grains and delicate structures such as microfossils or microbiota and thus has considerable application within the petroleum industry, for example, for the paleontological dating of marine sediments.

In SEM an electron beam is rastered across the surface of a specimen to build up a picture of the entire area. Electrons are used because they have a much shorter effective wavelength than visible light and therefore provide much higher resolving power (Lapidus, 1990). The microscope operates by counting the secondary electrons emitted when the primary electron beam strikes and excites atoms at the specimen's surface which is generally coated with a thin film of gold or carbon. The secondary electrons are detected by a scintillation counter which produces a voltage signal proportional to the number of electrons emitted from the specimen surface. The quantity of electrons emitted is governed by the specimen's surface morphology which results in signal strength variation from the surface profile of the specimen. The signals are then amplified and used to produce an image on a monitor.

Many scanning electron microscopes have an associated analytical facility. The most common of these is Energy Dispersive X-ray Spectrometry (EDS) which is based on detecting the X-ray energy spectrum characteristics of the elements present in the area of electron beam impact. This technique combined with SEM makes it possible to identify elements *in situ*.

Although the use of SEM has increased steadily since its commercial introduction in the 1960's, the amount of reference material available to aid in SEM mineral identification is relatively small (Welton, 1984). Texts such as that by Hearle *et al.*, (1972) and Wells (1974) give excellent descriptions of SEM theory but information regarding the application of SEM to geological studies is often very limited in contrast to biological studies. Whilst Hearle *et al.* (1972) provide an excellent review of the application of SEM to metallurgy, the literature is heavily biased towards industrial applications, such as the detection of metal fatigue, stress fractures and surface wear studies. Welton (1984) published an atlas to provide SEM users in the petroleum industry with a guide to aid in the identification of minerals which are commonly found in clastic reservoir rocks. Because the atlas was almost exclusively designed for use within the petroleum industry it was of limited use in this present study.

Over the past decade the use of SEM and EDS in geological and pedological related studies has steadily increased as researchers have begun to incorporate these technologies into their repertoire of analytical techniques. For example, Goenadi & Tan (1991), Robertson & Eggleton (1991) and Watanabe *et al.* (1992), have used SEM in studies to investigate the weathering of clay minerals such as muscovite, kaolinite and montmorillonite. In these studies SEM (and EDS in the first two studies) was used in conjunction with other analytical techniques to identify and characterise various primary and secondary clay minerals and to investigate weathering processes. SEM analyses were also used in a pedological study by Karathanasis (1991) to investigate phosphate mineral weathering in Alfisols developed in limestone. In this study SEM was used to study apatite surface weathering and to investigate the formation of secondary Ca-Al and Al and/or Fe-phosphates. Golden *et al.* (1991) have similarly used SEM and EDS to investigate phosphate dissolution in soils.

In a recent study by Inskeep *et al.* (1993), the surface morphology and secondary coatings of naturally weathered oligoclase grains in soils, sediments and rocks were characterised using SEM and EDS. The aforementioned techniques were used to characterise etch pits and secondary coatings on a sequence of oligoclase grains at various stages of weathering. The results were used to evaluate the efficiency of laboratory studies in predicting weathering intensities in natural watersheds.

In four notable studies investigating pyrite oxidation, SEM was used to elucidate the role of *Thiobacillus ferrooxidans* (Bennett & Tributsch (1978); Keller & Murr (1982); Rodriguez-Leiva & Tributsch (1988) and Mustin *et al.* (1992). In the study of Rodriguez-Leiva & Tributsch (1988) *T.ferrooxidans* was cultivated on synthetic pyrite and SEM was used to examine the morphology of the pyrite-bacteria interface with time. SEM facilitated the identification of bacterial corrosion pits at various stages of development and helped to identify the presence of organic films in and around corrosion pits created by the bacteria. The organic compounds found between the bacterial outer membrane and the sulphide

interface are believed to be secreted by *T.ferrooxidans* during sulphide oxidation to facilitate breakdown of the sulphide moiety.

Rodriguez-Leiva & Tributsch (1988) believed that previous SEM studies of *T.ferrooxidans* on natural sulphide surfaces were largely unsuccessful due to the complex surface morphology of non-synthetic sulphide crystals. Research aided by SEM indicates that *T.ferrooxidans* does not absorb randomly onto pyrite but instead preferentially attacks crystal defects, impurities and mineral inclusions on the crystal surface (Andrews, 1988). Based partially on SEM analyses, Rodriguez-Leiva & Tributsch (1988) suggested that *T.ferrooxidans* has some sort of “chemotactic” sense which allows them to locate a favourable site for attachment on the sulfide interface. *T.ferrooxidans* is thought to be able to distinguish between surface areas that mechanically or chemically deviate from ideally crystalline sulphide substrates (Bennett & Tributsch, 1978). Research outlined by Natarajan (1990) also indicates that surface defects, crystallographic orientation and surface heterogeneity are the main parameters influencing bacterial corrosion patterns on sulphide minerals.

Mustin *et al.* (1992) applied SEM in an investigation of bacterial oxidation of pure pyrite by *T.ferrooxidans*. Pyrite samples were biologically leached over a 60 day period to evaluate elution front analysis of intragranular porosity. SEM microphotographs of individual pyrite grains indicated that after the 60 day period a great number of corrosion tunnels were created by the bacteria, resulting in a surface area increase of approximately 42%. Further analysis of the sulphide particles indicated that some 25 km of tunnels were formed as a result of pyrite dissolution by *T. ferrooxidans* per gram of pyrite. The mean diameter of tunnels was of the order of 2 μm and the shapes were predominantly hexagonal or square, probably relating to the cubic lattice of pyrite (Keller & Murr, 1982). The corrosion tunnels showed preferred orientation, evidenced in microphotographs by the anisotropic parallel alignment of pores. SEM images of the burrow borders showed little sign of bacterial or chemical degradation indicating the reactive area is located at the base of the holes.

In a study investigating the oxidation of pyrrhotite (Fe_{1-x}S), SEM was used to obtain images of biologically oxidised mineral surfaces (Kwong *et al.*, 1995). SEM revealed that the bio-oxidised pyrrhotite surfaces are appreciably different to pyrite surfaces in that they are characterised by micro-fractures and circular deposits of what was believed to be bacterially generated elemental S.

The recent studies of Willet *et al.* (1992) and Lin (1997) also provide useful examples of the application of SEM and/or EDS technology in studying the oxidation of sulphide minerals in acid sulphate soils and mine tailings, respectively. The study of Lin (1997) is similar to the present study in that it used SEM and EDS to complement more traditional analytical and mineralogical techniques (including FAAS and XRD) to characterise base-metal tailings.

5.3.1 Aims of SEM & EDS Study

Although FAAS, chemical and XRD data indicate that the surface tailings (0-200mm) contain comparatively low concentrations of metal-bearing sulphide minerals, it provided little insight into the original distribution of sulphide minerals in the profile. The primary aim of the SEM and EDS research reported in this chapter was to:- (1) establish if the distribution of sulphide minerals in the profile was originally relatively uniform with depth and (2) to investigate if the depletion of metals in the surface tailings resulted from sulphide oxidation and the subsequent leaching of soluble metal compounds. In addition, it was envisaged that SEM and EDS analyses would help identify a relationship between the Tui tailings chemistry, depth and surface morphology, should one exist.

5.3.2 Sample Preparation

As previously reported in section 5.1.3, XRD analyses of the six 100-mm incremental tailings samples indicated they were composed primarily of quartz and kaolinite. To isolate sulphide particles for SEM inspection and EDS analyses, sodium polytungstate (SPT) was again used to separate the majority of quartz and kaolinite from the heavy mineral fraction (sulphide component) of the tailings samples as per the method outlined in section 5.2.1

(Callahan, 1987). The separation method was this time conducted using unground tailings samples. Thus additional care was taken to ensure loosely bound aggregates were adequately broken apart to facilitate dispersion of the particles in solution.

Samples of the heavy mineral fraction of the tailings were mounted on aluminium stubs and sputter-coated with gold. The use of highly conductive gold for sample coating minimises static electricity build up and thus minimises ‘flaring’ and improves image quality. In total, seven samples were mounted for SEM examination, including six tailings samples and a specimen of ground (<150 µm) Tui ore (Table 5.4).

Table 5.4 Tailings Samples Examined by SEM & EDS.

Sample	Depth [mm]	SEM	EDS	HM [%]
1	0-100	✓	✓	1.45
2	100-200	✓	✗	1.55
3	200-300	✓	✗	7.23
4	300-400	✓	✗	8.11
5	400-500	✓	✗	9.85
6	500-600	✓	✓	16.25
Tui ore	NA	✓	✗	77.7

(✓ = analysis conducted, ✗ = analyses not conducted, NA = not applicable)

For EDS analysis two samples were sputter-coated with carbon instead of gold. Although carbon-coated samples generally produce an inferior SEM image to gold-coated samples (attributed to carbon’s poorer conductive properties) it is more suited to EDS analysis as it prevents the masking of the X-ray spectra back-scattered from the samples. Tailings from the 0-100 mm and 500-600 mm depths were chosen for EDS analysis because, (i) XRD analyses indicated that there was a relatively large difference in sulphide content between the two samples, (ii) chemical characterisation of the tailings indicated that they were quite dissimilar in terms of their pH, sulphate and metal content and theoretical acid generating potential and (iii) field observations indicated that these samples were obtained from contrasting oxidising environments.

5.3.3 Scanning Electron Microscopy Method

SEM examination and EDS analyses of the samples were made with a Cambridge Stereoscan 250 Mark 3, with an attached Link E5431 EDS detector and 8 µm beryllium window. Fine-grained black and white micrographs of the mineral surfaces were taken using a 35-mm Nikon camera focused on a high-definition monitor. Exposure times of 60 seconds were used to maximise the signal to noise ratio and to improve image quality.

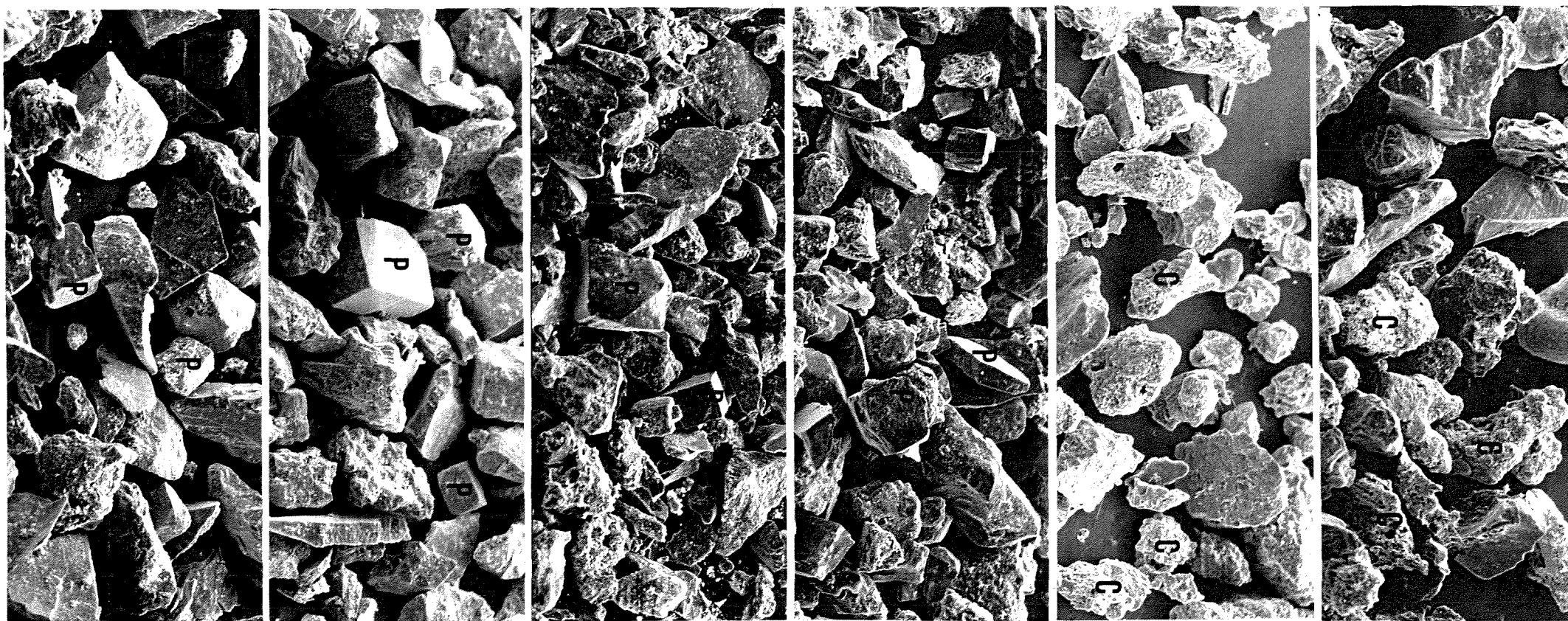
5.3.4 Results & Discussion

5.3.4.1 Scanning Electron Microscopy

SEM examination of HMF samples provides evidence that the change in the distribution of sulphide minerals with depth is attributable to differences in the extent of oxidation and subsequent dissolution of sulphide minerals. Sulphide particles in the upper 200 mm of the profile generally exhibited very irregular and craggy morphologies (Plate 5.1). In contrast many of the mineral grains between 200 and 600 mm depth exhibited angular well-defined edges which enabled their crystal habit to be readily recognised. EDS analysis conducted on several cubic particles yielded spectra that were characterised by two Fe peaks and a single S peak (Appendix 5(A)). Comparison of these spectra with that of a standard iron pyrite (FeS_2) spectrum confirmed that the cubes were indeed pyritic (Welton, 1984).

Cubic pyrite particles were observed only in the 200-600 mm zone and became more prevalent towards the bottom of the profile (Plate 5.1). Under moderate magnification (420x) pyrite cubes isolated in the 500-600 mm depth sample show few signs of 'weathering' (Plate 5.2). At higher magnification, however, there is some evidence that dissolution of the mineral edges has occurred (Plate 5.3). The lack of cubic pyrite in the upper 200 mm of the tailings profile indicates that this form of pyrite is susceptible to oxidation and has been 'weathered' beyond recognition.

The effects of surface weathering of a pyrite particle isolated in the 300-400 mm zone is evident in Plates 5.4 & 5.5. Small hexagonal shaped etch holes are clearly visible in the middle and upper left hand corner of Plate 5.5 The most probable mechanism for the



600 mm Depth

Surface

Plate 5.1 A photo-mosaic of six microphotographs correlating to each of the sampling depths from 0-600 mm. Particles within the top 200 mm of the profile are generally seen to exhibit a craggy and irregular morphology (C). The occurrence of cube-shaped pyrite minerals (P) and angular grains is seen to increase with depth (Magnification 180 x).

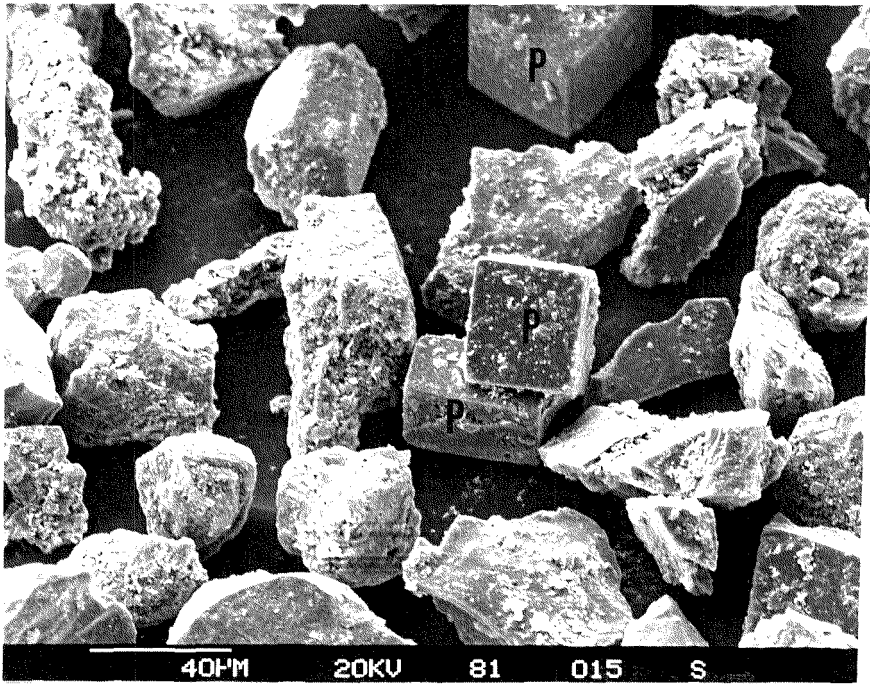


Plate 5.2 A SEM image showing three cuboidal pyrite grains (P) isolated in the 500-600 mm zone. Their well defined cube shape indicates that they are resistant to the micro-environmental weathering conditions prevailing at this depth (Magnification 470 x).

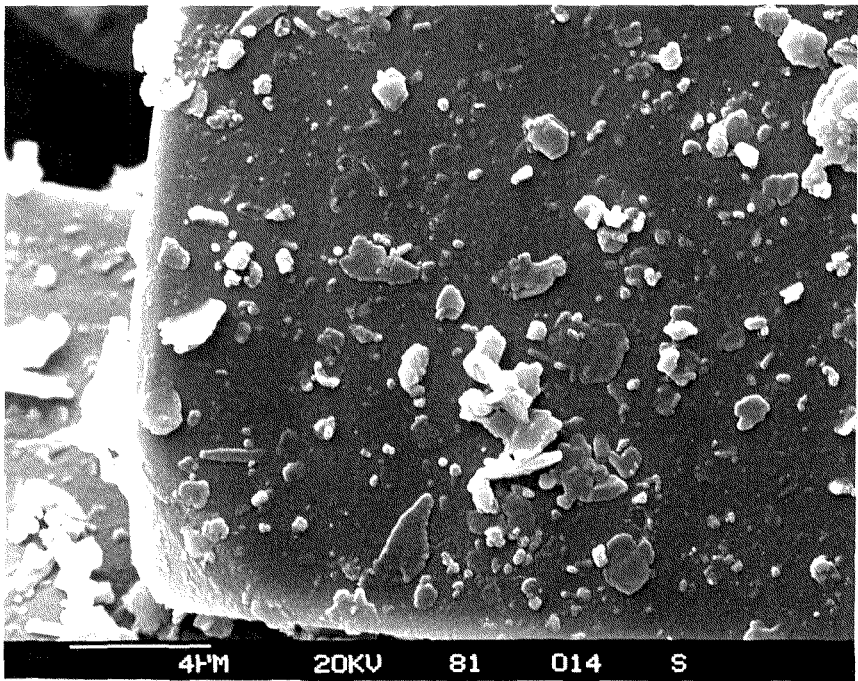


Plate 5.3 A magnified view of central pyrite cube in Plate 5.2 confirms that the surface is largely unweathered and that it is partially coated with plates of kaolinite (Magnification 4700 x).

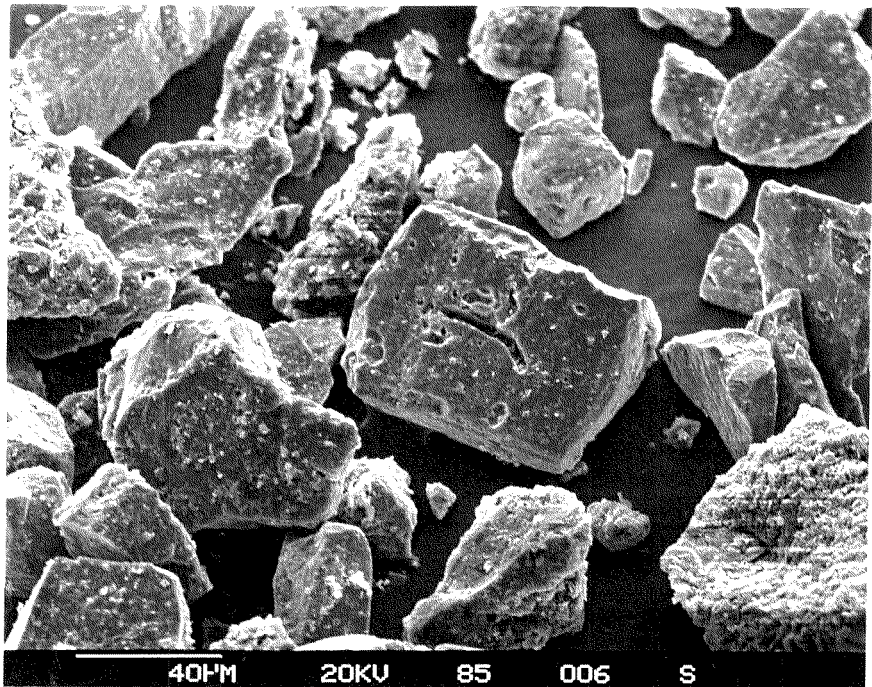


Plate 5.4. Surface etching of a pyrite grain (centre) indicates that limited biochemical oxidation is occurring at 300-400 mm depth (Magnification 480 x).

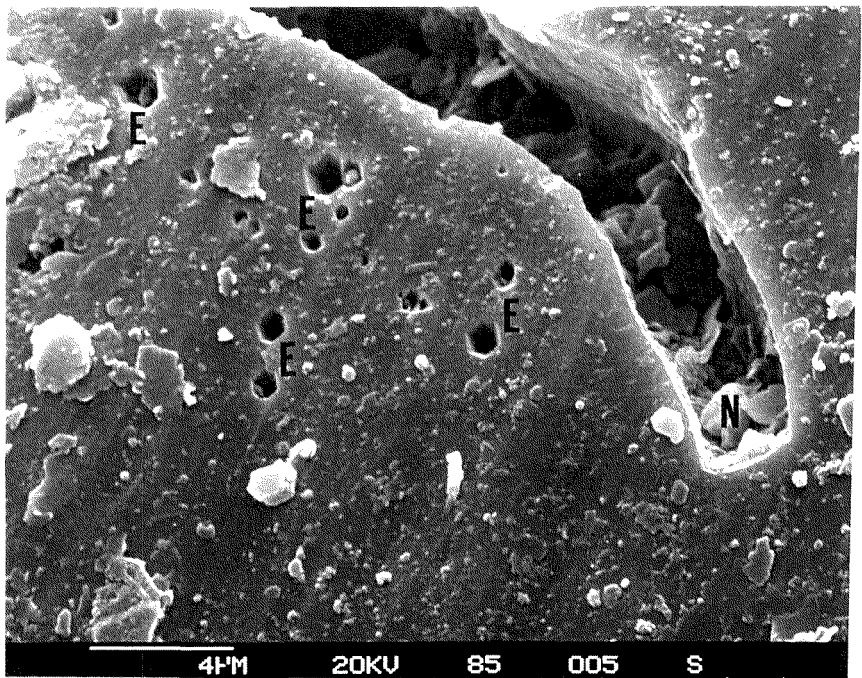


Plate 5.5 A magnified view of the pyrite grain in Plate 5.4 indicates the presence of several small hexagonal etch holes (E). Like the smaller holes, the larger non-symmetrical etch pit (N) is thought to have resulted from biological and/or chemical oxidation of the pyrite along a chemically active zone (Magnification 4800 x).

creation of these holes is that they are the result of bacterial and/or chemical oxidation of the pyrite. Similar hexagonal etch-pits were observed in SEM microphotographs from an experiment investigating the role of crystallographic orientation in pyrite oxidation (Keller & Murr, 1982). Hexagonal and sub-hexagonal etch pits in pyrite were also observed with SEM in research conducted by Mustin *et al.* (1992). In the latter study the etch pits were believed to have formed as a result of bacterial oxidation, with the hexagonal shapes and anisotropy of the corrosion pits being related to the cubic lattice of pyrite.

Burrow-like weathering parallel to the mineral surface is also evident in Plate 5.5. The irregular shape of the etch pit indicates that preferential weathering of the mineral may have occurred at a chemically active zone. Such zones are believed to result from crystal dislocations or fracture lines in the mineral which enhance the rate of sulphide oxidation by providing conduits for the diffusion of S atoms (Andrews, 1988). Bacteria adsorbed at these sites are thought to be advantaged because S oxidation has a much higher yield of free energy than Fe oxidation (Andrews, 1988). At pure pyrite sites the diffusivity of S atoms through pyrite crystals is several orders of magnitude lower. This is a possible explanation of the observed selectivity shown by *T. ferrooxidans* for specific sites (Bennett & Tributsch, 1978; Andrews, 1988; Rodriguez-Leiva & Tributsch, 1988; Mustin *et al.*, 1992). Wiggering (1993) reported similar leaching channels in pyrite which he suggested resulted from the selective dissolution of individual zones within the crystals. An alternative explanation for the formation of the irregular etch-hole, however, is that it may have resulted from the release of surface fluid inclusions during pyrite dissolution.

Although the surface tailings (0-200 mm) were devoid of cubic pyrite they were found to contain a greater proportion of distinctive 'aggregate grains' than the underlying tailings (Plates 5.6 & 5.8). At high magnification (9200x) these grains are seen to be composed of individual sub-angular crystals less than 1 μm in width (Plate 5.7). EDS analysis of an aggregate grain isolated in the 0-100 mm zone indicated that it comprised primarily Al, Cu, Fe, Pb, Si and S (Appendix 5(B)). Although the dominant form of the S present in the particle (ie. sulphide or sulphate) could not be interpreted from the EDS spectrum for the

mineral, it is highly unlikely that tiny sulphide crystallites would persist in the strongly oxidising conditions present in the surface tailings. These particles were therefore postulated to be clusters of metal sulphate crystallites precipitated from the weathering solution. XRD and chemical analysis of the 0-100 mm samples indicates that anglesite is likely to be a major constituent of the grain, however, this could not be confirmed from the EDS spectra due to the major EDS peak for Pb coinciding with that of S (Appendix 5 (B)).

SEM examination of the HMF of the tailings indicated that all the samples again contained appreciable proportions of quartz after density separation (Plate 5.9). Although quartz's characteristic conchoidal fracture and absence of cleavage made visual identification of particles relatively straightforward (O'Donoghue, 1976), the composition of these grains was confirmed using EDS. Whilst the quartz (SiO_2) spectra were dominated by a single silicon peak, minor Al, Fe and Sn were identified in several samples (Appendix 5(C)). As discussed in section 5.2.3 the inability of the heavy mineral separation method to completely segregate quartz from the HMF was explained by the presence of sulphide inclusions in the quartz grains.

EDS analyses confirmed the presence of phyllosilicate clay minerals in the tailings. It appears that X-ray amorphous iron-alumino-silicate gels were also present as coatings on some grains in the surface tailings (0-100 mm). EDS spectra associated with these grains exhibited large Fe peaks with relatively small S peaks, indicating that the Fe was not intimately associated with S in the form of a sulphide or sulphate compound but rather with Al, Si and presumably O_2 (Appendix 5 (D)). The detection of iron-alumino-silicate gels in the tailings is significant in that it is indicative of strong oxidising conditions which are conducive to sulphide oxidation.

A potential source for the Al and Si identified in these spectra is the clay mineral kaolinite. Although kaolinite was readily detected in the samples by XRD analyses, well crystallised kaolinite was difficult to identify in the SEM microphotographs. Some of the mineral

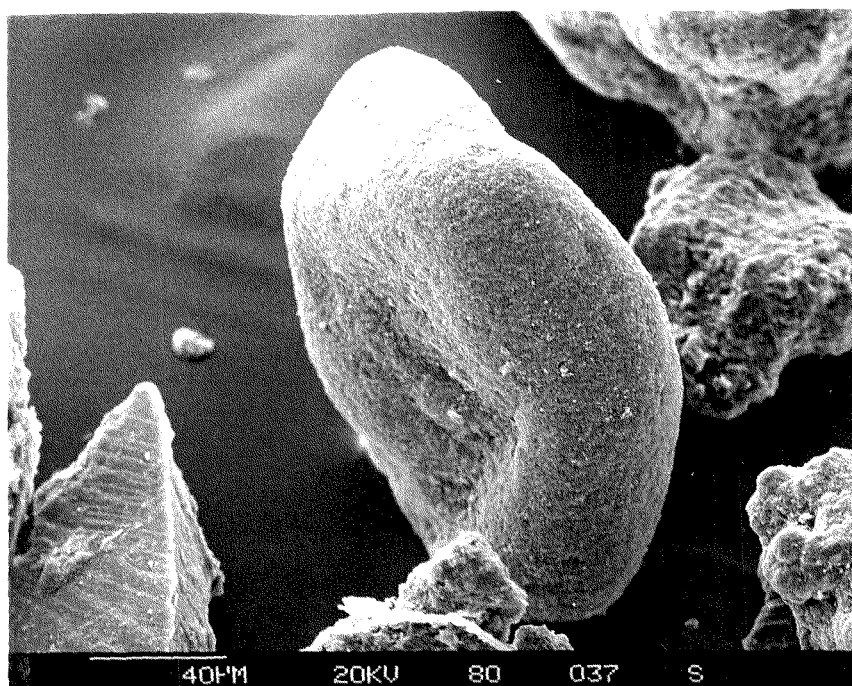


Plate 5.6 An 'aggregate grain' comprised of sub-cuboidal crystallites isolated in the 0-100 mm depth zone. These distinctively shaped grains are more prevalent in the surface 200 mm of the profile (Magnification 470 x).

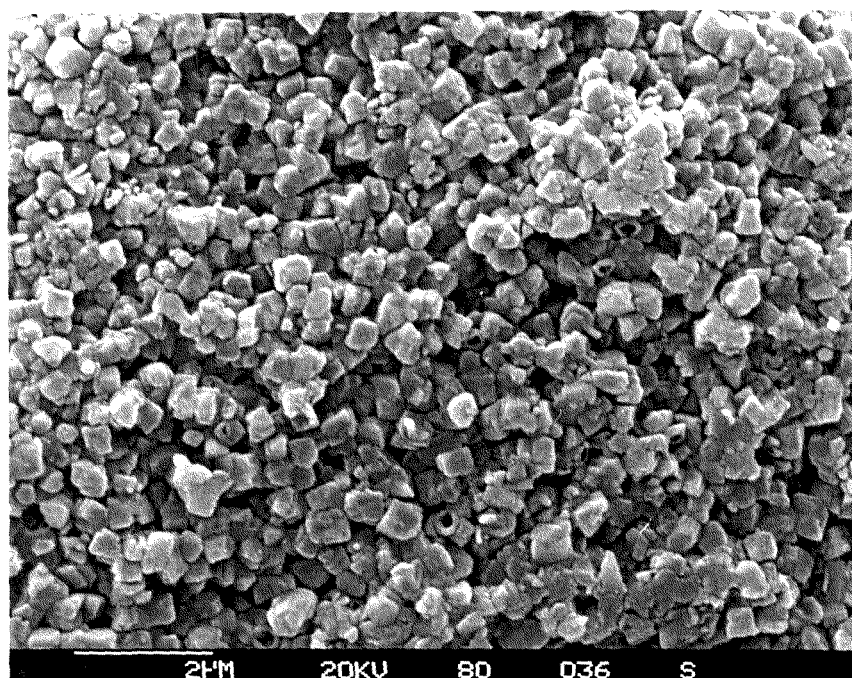


Plate 5.7 A magnified view of the sub-cuboidal crystallites constituting the aggregate grain in Plate 5.6 (Magnification 9200 x).

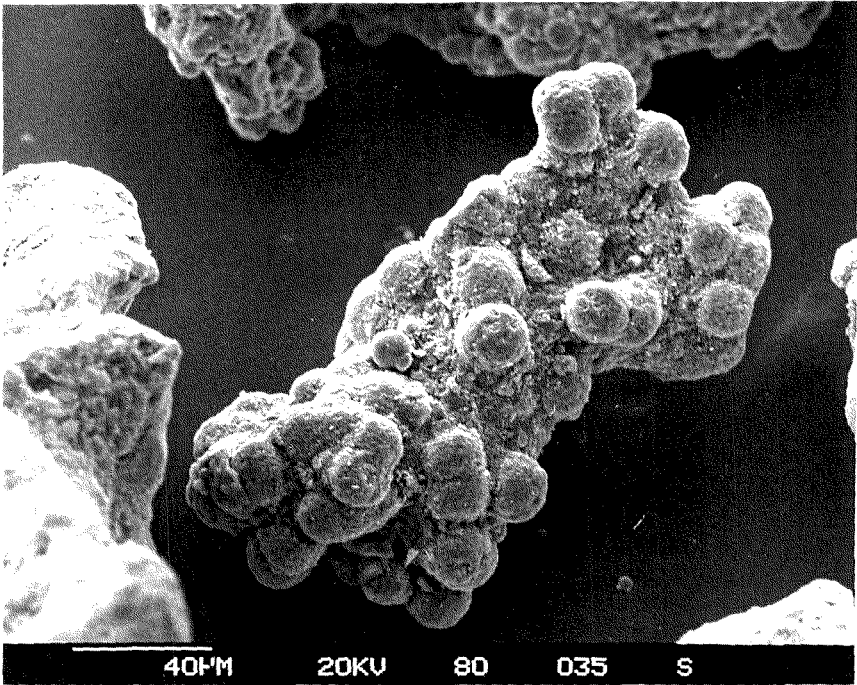


Plate 5.8 An ‘aggregate grain’ isolated in the 0-100 mm depth zone exhibiting mamillary growth habit (Magnification 460 x).

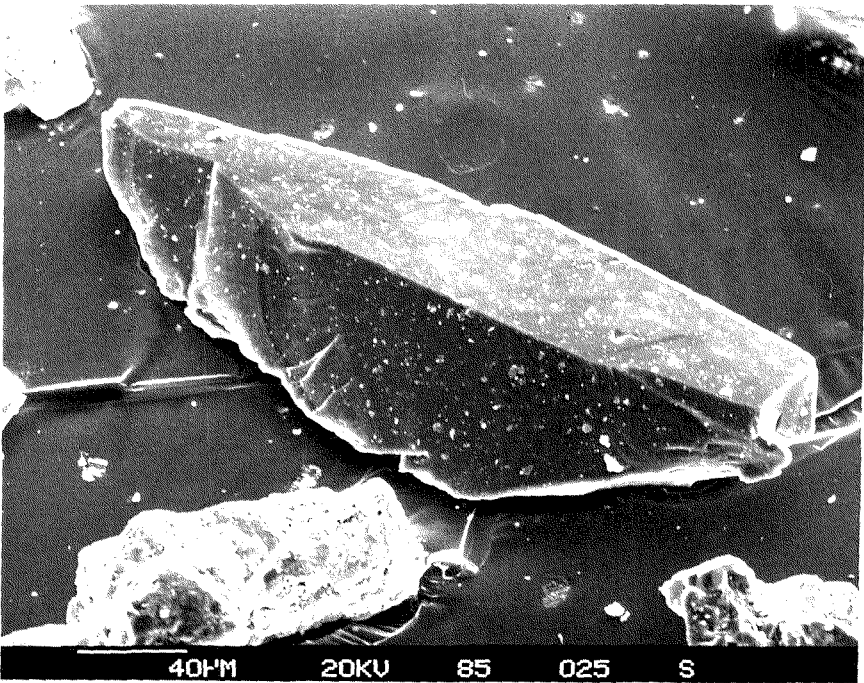


Plate 5.9 A SEM image of a quartz particle ‘contaminating’ the heavy mineral fraction of the tailings. Quartz particles such as these constitute > 80 - 90% of the tailings and are characterised by conchoidal fracturing and angular morphologies (Magnification 360 x).

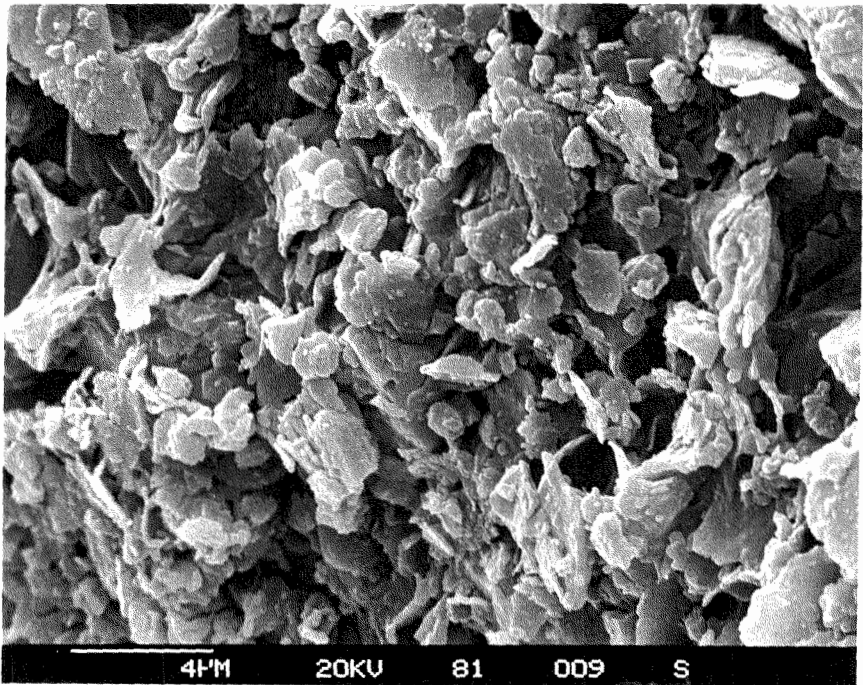


Plate 5.10 A high resolution image of plate-like kaolinite located on the surface of a mineral grain in the 500-600 mm sample (Magnification 4700 x).

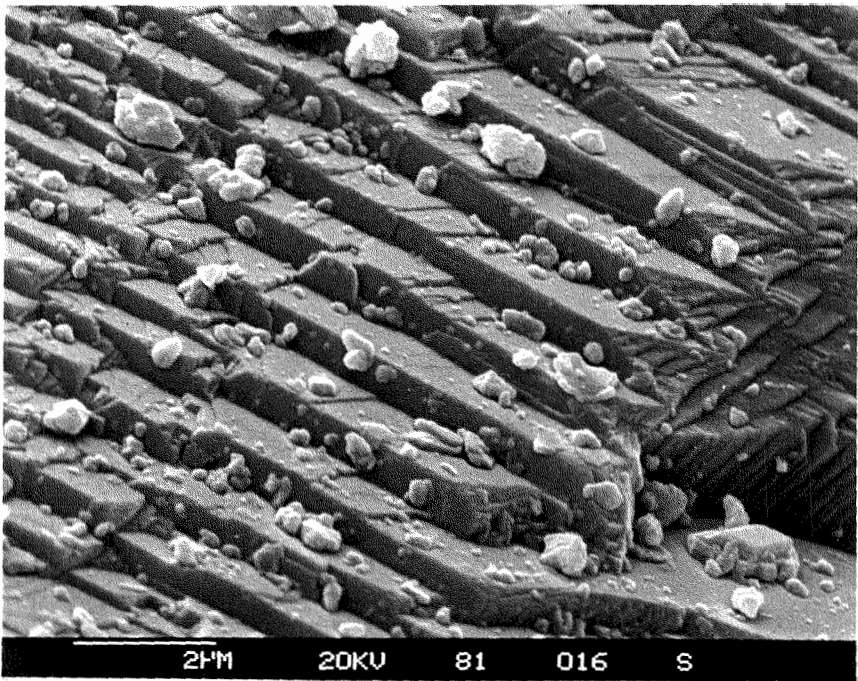


Plate 5.11 A SEM microphotograph of the surface of a sulphide mineral isolated in the Tui ore sample (Magnification 9500 x).

surfaces were, however, coated with plate-like particles which based upon their size and morphology were probably kaolinite (Plate 5.3 & 5.5). Increased magnification of selected mineral grains revealed what appeared to be localised ‘pockets’ of poorly crystallised kaolinite (Plates 5.10). It is possible that the kaolinite flakes were difficult to identify because they had undergone partial dissolution as a result of edge attack under the acidic conditions prevailing in the tailings (Barnhisel *et al.*, 1982).

SEM images of the Tui ore were characterised by highly angular particles. Whilst the majority of the grains were indistinctive, some grains exhibited unique cleavage patterns (Plate 5.11)

5.3.5 Low Magnification Energy Dispersive X-ray Spectrometry

EDS analyses confirmed the findings of XRD analysis which indicate that the tailings contain a variety of minerals. This finding was not unexpected given the multitude of minerals known to occur in the ‘parent material’ (the Champion and Ruakaka ore bodies) from which the tailings were derived (Courtney *et al.*, 1990; Wodzicki & Weissberg, 1970; Weissberg & Wodzicki, 1970).

A total of 12 elements were detected in the tailings by EDS including Al, Ba, Ca, Cu, Fe, K, Pb, S, Si, Sn, W and Zn. Whilst tungsten (W) may be an artefact of the sodium polytungstate used to separate the minerals fractions, wolframite $\{(\text{Fe}^{2+}, \text{Mn})\text{WO}_4\}$ has been identified in the ore body and thus W may be a ‘genuine’ elemental constituent of the Tui tailings (Courtney *et al.*, 1990).

Low magnification EDS analyses were conducted on the two samples to establish if there was any marked variation in the elemental composition of the tailings. Three EDS analyses were conducted at each depth at 180 x magnification. Although minor differences were noted between the replicate EDS spectra, the differences were negligible compared to those between the two sampling depths. EDS analyses of the 0-100 mm sample (Appendix 5(E)) indicated that it contained no Cu or Zn but small quantities of Ba presumably in the form of

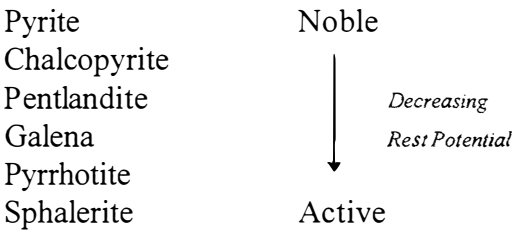
barite (BaSO_4) which is a common constituent of hydrothermal vein deposits (O'Donoghue, 1976). In contrast, the 500-600 mm tailings sample contained Cu and Zn but no Ba (Table 5.5; Appendix 5(F)). Trace quantities of Ca were also identified in the surface sample.

Table 5.5 EDS analysis of Tui tailings particles

Depth [mm]	Al	Ba	Ca	Cu	Fe	K	Pb	Si	S	Sn	W	Zn
0-100	✓	✓	✓	✗	✓	✓	✓	✓	✓	✗	✗	✗
500-600	✓	✗	✗	✓	✓	✗	✓	✓	✓	✗	✓	✓

The absence of EDS detectable Cu and Zn in the upper sample (0-100 mm) reflects the fact that the sulphide minerals associated with these metals are more susceptible to weathering than pyrite. Research has shown that galvanic interactions come into play in poly-sulphidic leaching systems (Natarajan, 1990). These interactions lead to the preferential weathering of electrochemically active sulphide minerals due to the formation of galvanic cells (Natarajan, 1990; Kwong, 1995). Table 5.6 lists six base-metal sulphides in a bioleaching medium, in order of decreasing stability based on their relative electrochemical activity. Table 5.6 shows that pyrite and chalcopyrite are relatively ‘noble’ sulphides and are thus more difficult to oxidise in an acid medium than say pyrrhotite or sphalerite, which are electrochemically less stable.

Table 5.6 Galvanic series of some common sulphide minerals (adapted from Natarajan, 1990).



The galvanic dissolution process is driven by the potential differences existing in a galvanic couple, while the rate of anodic oxidation is a function of the galvanic current flowing in the circuit (Natarajan, 1990). The rate at which selective dissolution of sphalerite in the presence of cathodic pyrite for example, depends on several factors such as the rest

potential differences and conductivity of the minerals, the relative surface areas of the anodic and cathodic minerals, the distance between the sulphidic electrodes, the duration of mineral contact, the environmental parameters of the medium (eg. pH, Eh and oxygen availability) and the presence and activity of acidophilic bacteria such as *T. ferrooxidans* (Natarajan, 1990).

The phenomenon of selective galvanic bioleaching is one possible explanation why Cu and Zn were not detected in the upper tailings sample by EDS and may partially explain the absence of XRD detectable galena in the 300-400 mm tailings zone. The greater concentration of pyrite in the tailings and the cathodic protection afforded to this mineral by galena and sphalerite has undoubtedly contributed to the selective oxidation of the less noble sulphides in the upper profile. Sphalerite is particularly electrochemically unstable due to its low (negative) rest potential and thus tends to be rapidly oxidised and 'lost' from polysulphidic materials (Natarajan, 1990; Kwong, 1995)

Although the distribution of Cu, Fe, Pb and Zn within the tailings profile is readily explained by the solubility of the oxidation products and/or the electrochemical reactivity of the sulphide minerals, the reason for the low concentrations of Ba at depth is unknown. Like Pb, Ba is immobile over most of the Eh-pH field of water and tends to form highly insoluble sulphate (BaSO_4). Although BaSO_4 dissociates to form Ba^{2+} below pH 1.2, the pH and Eh conditions present at 500-600 mm depth are not thought to be conducive to the formation of this cation (Brookins, 1988). In fact, Ba is more likely to be immobile in the conditions prevailing at the 500-600 mm depth than it is in the considerably more acidic conditions present in the surface tailings (0-100 mm). It is thus postulated that the surface tailings were derived from ore containing relatively high concentrations of barite and that this mineral has remained *in situ* due to its chemical stability. Presumably Ba may have also undergone some isomorphous substitution with sulphate-bound Pb in the surface tailings. Oxidation of sulphide minerals in the top 200 mm of the profile is also likely to have resulted in the selective enrichment of barite due to the leaching of soluble metal compounds from the upper profile. The absence of XRD detectable concentrations of barite

or other Ba-bearing minerals, however, indicates that this element is not a major constituent of the tailings at either depth.

Comparison of the EDS spectra for the respective surface (0-100 mm) and subsurface (500-600 mm) samples indicates that Pb concentrations are slightly higher in the surface sample (Appendices 5(E) & 5(F)). This trend is consistent with finding of XRD and FAAS analyses of the tailings.

5.4 Chapter 5 Summary & Conclusions

- XRD analyses of the Tui mine tailings indicate that they are composed primarily of quartz, with subordinate kaolinite and pyrite. Sodium polytungstate (SPT) density was required to facilitate the identification of several additional minerals including; chalcopyrite, galena, sphalerite and anglesite.
- Cross contamination of the heavy and light mineral fractions of the tailings with quartz and sulphide minerals respectively, continued to hamper mineral identification after SPT density separation. Contamination of the samples was explained by examination of the tailings particles under an optical microscope which showed that a significant portion of the quartz grains were found to contain inclusions of sulphide minerals.
- Quantification of the light and heavy mineral fraction of the tailings after SPT density separation demonstrated a general trend of increasing heavy mineral concentration with depth. On a mass basis the tailings increased from about 1.5% heavy minerals near the surface to over 16 % in the 500-600 mm depth zone.
- The results gained from XRD analysis and sodium polytungstate separation of the Tui mine tailings were found to substantiate analytical data from the chemical characterisation of the tailings that indicates substantial oxidation of the tailings has occurred in the top 200 mm of the profile (Chapter 4). Supporting observations include; (1) the general increase in heavy mineral concentration with depth as determined by SPT density separation, (2) the lower abundance of sulphide minerals in the upper profile as evidenced by variations in XRD peak height intensity, (3) the absence of pyrite and/or

sphalerite in the LMF of the tailings derived from the upper 200 mm of the profile and (4) the greater concentrations of anglesite near the profile's surface.

- The identification of the highly insoluble anglesite in the tailings profile explains why Pb has remained largely *in situ* in the upper profile despite the strong leaching conditions.
- The major limitation of using XRD analyses to identify the mineral constituents of the Tui mine tailings was that the similarity of the XRD spectra for pyrite and sphalerite. Several coincidental d-spacings for these minerals limited the use of XRD to quantify the relative concentrations of these minerals in the tailings based on peak intensity.
- As hypothesised, SEM indicated that sulphide minerals in the top 200 mm of the tailings profile are significantly more weathered than those below 200 mm. The increased degree of weathering in the top 200 mm of the profile is reflected by:- (1) the very craggy and extremely irregular morphology of the grains, (2) the absence of cubic and angular shaped sulphide minerals and (3) the presence of a greater proportion of what are postulated to be aggregated sulphate minerals.
- SEM results indicate that the original distribution of sulphide minerals in the tailings profile was relatively uniform and that depletion of Cu, Fe and Zn from the upper profile is attributable to the oxidation of sulphides and the subsequent leaching of their weathering products. The selective dissolution of chalcopyrite and sphalerite due to galvanic interactions is postulated to have played a role in selectively depleting these minerals from the upper profile.
- The greater abundance of Pb and Ba in the upper profile is believed to result from a combination of:- (1) selective enrichment, as other more mobile metal compounds are oxidised and leached from the profile and/or (2) the possible deposition of Pb and Ba enriched tailings towards the end of mining operations.
- EDS analyses of the HMF of the tailings indicates that the particles tend to vary considerably in elemental composition, a finding believed to reflect the complex geochemistry of the Champion and Ruakaka ore bodies.
- Both SEM and EDS proved useful tools in assessing, qualitatively, the extent of weathering that has occurred in the tailings as a function of depth. There is undoubtedly

such scope for the use of these tools in characterisation and weathering studies of tailings and mine wastes.

Chapter 6

Lime Incubation Experiment

6.0 Introduction

It is well recognised that traditional tests for assessing the liming requirements of soils which involve short term pH buffering experiments (Peech, 1965; McLean, 1973) often seriously underestimate the requirements of pyrite-bearing materials (Berg, 1978; Caruccio *et al.*, 1988). Whilst the application of lime at rates sufficient to elevate pH to circumneutral levels may ameliorate acidity and decrease the bioavailability of heavy metals in sulphidic wastes in the short term, the effects are all too often temporary in nature. Reacidification of sulphidic growing media can occur extremely rapidly upon the exhaustion of added neutralising agents (Costigan *et al.*, 1981; Dent, 1986; Wiggering, 1993). Vegetation die-back often quickly ensues as phytotoxic metals remobilise and become increasingly available for plant uptake.

As discussed in Chapter 3 (section 3.4.1) ‘static tests’ have been specifically developed to assess the liming requirements and Acid Generating Potential (AGP) of sulphide-bearing mine wastes. These methods are commonly criticised, however, in that they fail to yield important information relating to the reactivity of materials in terms of their ability to produce and neutralise acid with time. For instance, static tests mostly fail to consider the effects and interactions of variables such as pH, oxygen concentrations, bacteria, grain size (surface area) and temperature. These and other parameters are known to significantly influence the rate of sulphide oxidation under field conditions (Sorensen *et al.*, 1980; Caruccio *et al.*, 1988, Kwong, 1995).

To elucidate the reactivity and AGP of mining wastes, kinetic tests are frequently conducted whereby samples are weathered under controlled conditions for periods of up to a year or more (Chapter 3; section 3.4.1.3). Several tailings and/or leachate parameters are generally monitored with time to gain an understanding of reaction kinetics. This chapter outlines the results of a simple kinetic experiment that was conducted on samples of the Tui mine tailings to assess the relevance of AGP prediction results obtained using static tests (Chapter 4; section 4.4). Furthermore, it was envisaged that the kinetic test outlined in this chapter would be useful in elucidating chemical and

mineralogical findings, reported in Chapters 4 and 5, that indicated that the surface tailings (0-200 mm) have undergone extensive oxidative-weathering and contain relatively low concentrations of acid generating sulphide minerals.

6.1 Aims & Hypotheses

The primary aim of the lime incubation experiment reported in this chapter was to assess the relative ‘reactivity’ of six tailings samples collected at 100-mm incremental depths (0-600 mm) in terms of their ability to oxidise and release acidity and heavy metals. It was anticipated that the results of this incubation experiment would confirm that the surface tailings are comparatively ‘inert’ and may be readily amended with low rates of lime (CaCO_3) to prevent reacidification. In contrast the subsurface samples (400-600 mm) and particularly the 500-600 mm sample, were predicted to be most reactive under aerobic conditions and thus most likely to reacidify after the application of liming materials.

An equally important objective of the experiment was to assess the efficacy of different rates of lime at preventing reacidification of the tailings and the release of selected heavy metals under conditions considered to be conducive to biochemical sulphide oxidation. The incubation experiment was therefore also aimed at quantifying the liming requirements of the tailings in terms of facilitating chemical conditions suitable for long term vegetative growth.

6.2 Experimental Design

A completely randomised, factorially designed incubation experiment was used to investigate the interaction of various liming rates on the selected properties of tailings (Table 6.1). Six liming rates were assessed, including a nil rate (control treatment) and five rates that were based upon the samples’ individual pH buffering capacities (see section 6.1.3.1). Each treatment was replicated four times.

Table 6.1 Design Treatments for Lime Incubation Experiment.

Liming Rates	Nil	½ pH-6	1 pH-6	2 pH-6	4 pH-6	8 pH-6
Depths	6	6	6	6	6	6
Replicates	4	4	4	4	4	4
Total	24	24	24	24	24	24

(Total Number of Samples: 6 depths × 6 liming rates × 4 replicates = 144)

6.3 Methodology

The Tui tailings material used for this incubation experiment corresponded to the six 100-mm incremental samples collected at grid sampling site 7 (Chapter 4; section 4.3.1.2). Approximately 15 kg of tailings were obtained at 100-mm sampling depths for the incubation experiment. Prior to lime addition the samples were air-dried and passed through a 2 mm sieve to break up loosely aggregated particles. The bulk samples were then thoroughly mixed and weighed out (400g sub-samples) into a series of numbered polyethylene bags to which the lime amendments were added.

6.3.1 Lime Application Rates

The 400 g tailings samples within the individual bags were treated with one of six rates of finely ground (<150µm) analytical grade calcium carbonate (lime). High quality, finely ground lime was used to ensure liming requirements were accurately met and that the effects of hydrous ferric oxide ‘armouring’ of limestone were minimised. The liming rates were based upon the pH buffering capacities of the samples, or more specifically, upon the amount of lime required to raise the pH of the samples to approximately 6.0 (1 pH-6 rate). This liming rate was estimated for each of the six 100-incremental samples using a short-term pH buffering experiment.

The buffering experiment (the methodology of which is outlined in Appendix 6(A)) was conducted over a 48 hour period and involved incubating 20g tailings samples with varying concentrations of dilute NaOH. The pH’s of the samples were plotted against NaOH concentrations to obtain sample-specific pH buffering curves from which the liming rates required to raise the pH of the samples to 6 (1 pH-6) were estimated.

None of the Tui tailings samples were anticipated to exhibit high pH buffering capacity¹ due to their negligible content of 2:1 clay minerals and organic matter. Although XRD analysis detected the presence of appreciable quantities of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) throughout the tailings profile, this 1:1 clay mineral develops very little surface charge via isomorphic substitution of Si^{4+} and thus exhibits low cation-exchange capacity (1-10 cmoles/kg) (Brownlow, 1979; Pierzynski *et al.*, 1994).

The results of the pH buffering experiment confirmed that the Tui tailings samples have little capacity to buffer against pH change, as indicated by the comparatively small volumes of dilute NaOH that were required to induce relatively large shifts in pH (Table 6.2). The pH buffering curves (Figure 6.1a) showed that there were differences in the initial pH (Y intercepts) and the rate of change in pH with hydroxide addition (slope) between the samples. Figure 6.1b indicates that a relationship between pH buffering capacity and sampling depth exists. Tailings obtained at lower depths within the profile were found to exhibit a greater capacity to resist pH change than surface samples. The difference was most pronounced between the 0-100 mm and the 400-500 mm samples which exhibited 1 pH-6 liming requirements of 1.17 and 7.00 Mg CaCO_3 /1000 Mg of tailings respectively (Figure 6.1b). This trend is believed to reflect a combined increase in the relative concentrations of fine-grained materials (silt and very fine sand), the pH buffering mineral kaolinite and most importantly hydroxide-consuming sulphide minerals with depth. It should be noted that variations amongst the initial pH of the samples also influenced the magnitude of the various 1 pH-6 liming requirement values presented in Figure 6.1b.

Tailings samples were also amended with lime at rates of nil, half, one, two, four and eight times the 1 pH-6 liming rate (Table 6.2). It was postulated that in the presence of high concentrations of acid generating sulphide minerals (ie. at sub-200 mm depths) the 1 pH-6 liming rate would be insufficient to maintain the pH of the tailings at circumneutral levels for the duration of the experiment. Thus, the higher liming rates

¹ The pH buffering capacity of a growing medium is an extremely important characteristic in that it has a significant bearing on the availability of nutrients and phytotoxic metals to plants. A material's capacity to buffer against pH change is largely governed by its clay and organic matter content, as these materials tend to have relatively high cation exchange capacities and thus have an inherent ability to release and absorb 'acidic' ions.

were included to try and identify an ‘optimum’ liming rate for the Tui tailings to maintain the pH for long term and to observe the effect of relatively high rates of lime on pH and availability of ‘plant available’ metals with time.

With the exception of tailing obtained from the 0-200 mm depth zone, it was found that the 8 pH-6 liming rate (the highest used in the incubation experiment) was substantially lower than those theoretically required to prevent eventual reacidification of the tailings² (Figure 6.2a). It was not, however, deemed necessary to treat subsurface (200-600 mm) tailings with rates of lime $\geq$ TAGP rate, as the 8 pH-6 liming rate was predicted to be sufficiently high to prevent the various samples from reacidifying within the short to medium term (ie. for the 1½ year period over which the experiment was run).

Table 6.2 pH buffering capacity, TAGP (theoretically acid generating potential) upper and lower limits and various liming rates based on the 1 pH-6 buffering rate.

Depth [mm]	pH Buffering *	TAGP †		Nil †	½ pH-6 †	1 pH-6 †	2 pH-6 †	4 pH-6 †	8 pH-6 †
		Lower	Upper						
0-100	15.6	6.6	10.0	0	0.59	1.17	2.34	4.68	9.36
100-200	22.8	8.2	12.4	0	0.88	1.75	3.50	7.0	14.0
200-300	24.4	75.4	113.9	0	1.47	2.94	5.88	11.76	23.52
300-400	26.3	75.8	114.3	0	1.71	3.41	6.82	13.64	27.28
400-500	55.2	71.4	108.2	0	3.50	7.00	14.00	28.00	56.00
500-600	53.9	113.0	171.0	0	3.16	6.32	12.64	25.28	50.56

* units = mmol OH⁻/kg/pH, † units = Mg CaCO₃/1000 Mg tailings

6.3.2 Water Regime

After lime incorporation the moisture content of the admixes were adjusted to approximately 70% of the 0.05 bar water content value³ using distilled water. The handling nature and aeration of the 200-300 mm, 300-400 mm and 400-500 mm samples was further improved by reducing the water content to between 60-65% of the 0.05 bar value (Table 6.3). Maintaining the samples in a moist but largely unsaturated condition^w as designed to provide conditions conducive to the biochemical oxidation of sulphide minerals constituting the tailings.

² As estimated by TAGP prediction outlined in Chapter 4 (section 4.4.2.1)

³ Determined using Haine’s apparatus.

Table 6.3 Percentage water content (oven dry basis) of the amended tailings at 0.05 bar pressure. 70% (0.05 bar) values and the approximate water content used in the Lime Incubation Experiment are also provided.

Depth [mm]	Water content at 0.05 bar	70% 0.05 bar content	Approx. Water Content Used
0-100	29.4 %	20.6 %	21 %
100-200	27.6 %	19.3 %	20 %
200-300	28.5 %	20.0 %	18 %
300-400	30.6 %	21.4 %	18 %
400-500	32.3 %	22.6 %	18 %
500-600	29.8 %	20.9 %	21 %

During the first 8 weeks of the experiment the water content of the samples were checked twice weekly and the admixes were aerated by trapping air within the polyethylene bags and vigorously shaking for 10 to 20 seconds. During the final stages of the experiment, the bags were watered and aerated once per week. Throughout the experiment an attempt was made to ensure that the ‘neck’ of the polyethylene bags remained open so as the samples were in contact with atmospheric oxygen. This practice was designed to enhance the aerobic oxidation of the tailings.



Plate 6.1 Lime Incubation Experiment January 1995.
Polyethylene bags containing lime amended tailings

6.3.3 Incubation Environment

During the lime incubation experiment the amended tailings samples were stored in a glasshouse maintained at an ambient temperature 25°C (Plate 6.1). The tailings were, however, subject to diurnal temperature variations of between 10-15°C in the glasshouse, particularly during the summer months. The polyethylene bags containing the amended tailings were arranged in randomised order and rotated weekly to minimise the positional effects within the glasshouse associated with temperature and lighting.

In laboratory leaching experiments Geidel (1979) demonstrated that the time interval between leaching events on pyrite does not affect the rate of pyrite oxidation. Pyrite is thus believed to convert to oxidation products at a constant rate independent of the concentration of oxidation products in the 'soil solution'. Burt & Caruccio (1986) suggested that this behaviour is expected of an irreversible process limited by the rate of the oxidation mechanism⁴. Geidel's (1979) research indicates that the use of a non-leaching environment in the present study may not have substantially effected the rate of sulphide oxidation.

6.3.4 Monitoring of the Treatments

The lime incubation experiment was commenced in July 1993 and terminated 76 weeks later (1 ½ years), in January 1995. During this time, periodic sampling was conducted to monitor pH and determine the concentrations of 'plant available' heavy metals with time. Sulphate ($\text{SO}_4^{=}$) levels were also assessed in the treated tailings 16 weeks after the commencement of the experiment (Table 6.4). The moisture contents of the samples were adjusted periodically to accommodate diminishing sample masses resulting from sub-sampling.

6.3.4.1 pH

The pH of the amended tailings in each of the 4 replicate bags was measured 13 times during the course of the experiment using a 1:2.5 tailings to water ratio as per the method outlined in Chapter 4 (section 4.1.1.1). To reduce processing time prior to sampling, the water contents of the amended tailings were adjusted to their required levels (60 to 70 % field capacity) and left to equilibrate for 30 minutes. Weight adjusted

sub-samples (the equivalent of 10.0 g of air-dried material) were then measured out into propylene beakers. Samples of standardised soil were included with each batch for comparative purposes.

6.3.4.2 Metals

Samples from 2 of the 4 replicate bags were analysed for concentrations of 0.1M HCl acid extractable Cu, Fe, Pb and Zn on four occasions during the course of the experiment (Table 6.4). The extraction was carried out according to the method outlined in Appendix 4(F) and the resulting supernatant solutions were analysed using a GBC 904AA atomic absorption spectrophotometer. Recommended standard slit width, flame types, lamp currents and wavelengths were used (Table 4.9).

6.3.4.3 Sulphate

The concentrations of 0.1M HCl acid extractable sulphate determined colourimetrically using an auto-analyser (Johnson & Nishita, 1952). Again, only 2 of the 4 treatment replicates were analysed.

Table 6.4 Sampling times for Lime Incubation Experiment.

	Weeks & Sampling Dates												
Parameter Measured	0 21.7.93	1 28.7..93	2 4.08.93	3 11.8.93	4 18.8.93	6 1.09..93	8 15.9.93	12 13.10.93	16 10.11.93	24 5.01.94	32 2.03.94	48 22.6.94	76 5.01.95
SO ₄ ⁼									✓				
Metals*	✓								✓		✓	✓	
pH	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

* Metals analysed include 0.1M HCl extractable Cu, Fe, Pb and Zn

⁴ See Chapter 3 (section 3.3.1) for discussion of sulphide oxidation and the rate determining reactions.

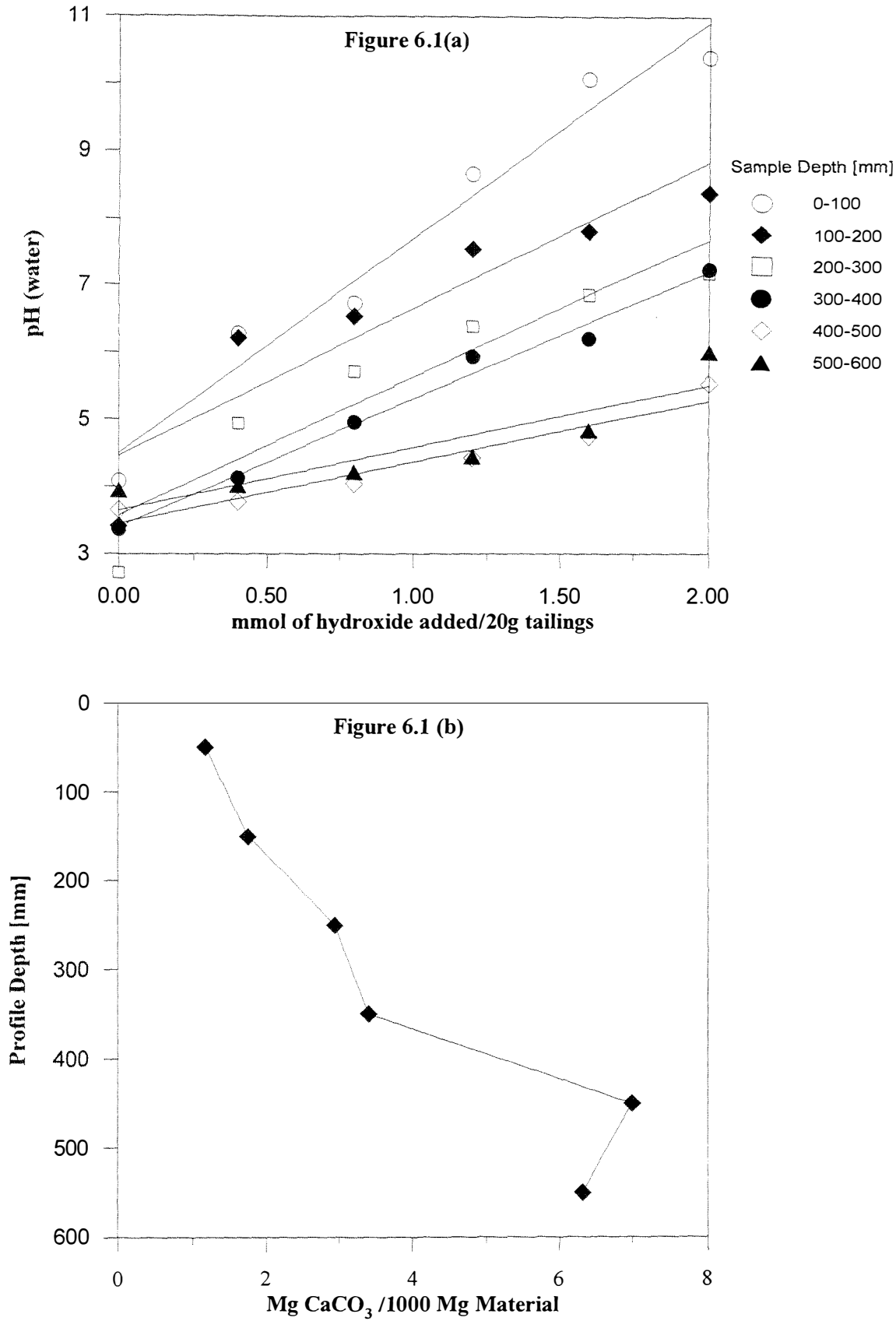


Figure 6.1 (a) pH buffering curves for tailings at various sampling depths.
(b) Relationship between profile depth and the amount of lime required to attain a pH of 6 at each depth increment. This figure clearly demonstrates that the pH buffering capacity of the tailings tended to increase with depth.

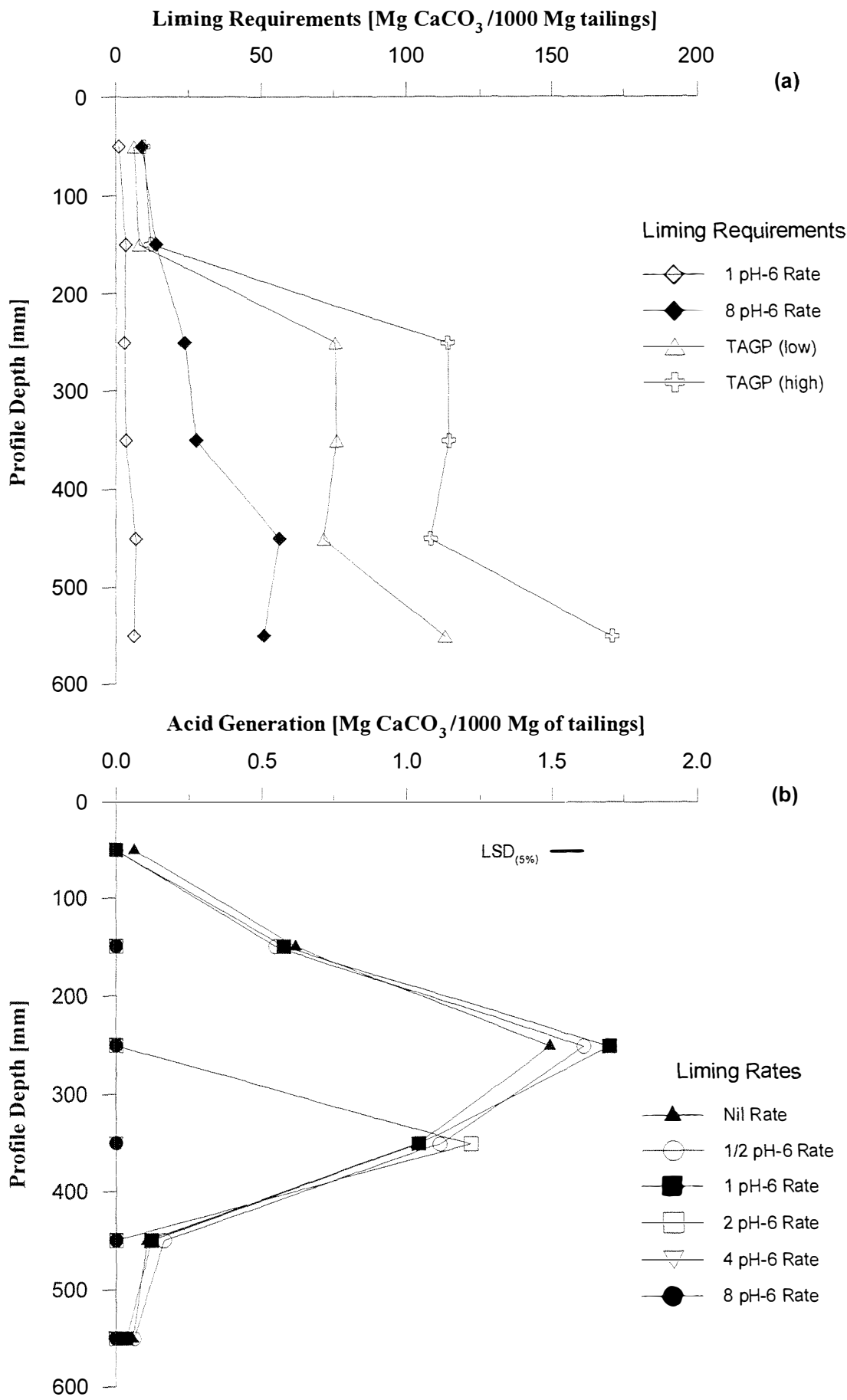


Figure 6.2 (a) Graph comparing Theoretical Acid Generating Potential (TAGP) and the rate of lime required to amend the pH of the tailings to 6.0 (1 pH-6 Rate). The 8 pH-6 rate represents highest rate of lime used in this trial. **(b)** Acid generated by the incubation samples over 76 week period calculated from hydrogen ion liberation.

6.4 Results

6.4.1 Variation in pH and Metal Levels with Time

6.4.1.1 pH

The pH versus time curves presented in Figures 6.3 and 6.4 clearly indicate that under non-leaching conditions H^+ ions were liberated from all control samples (non-limed) during the course of the experiment. The greatest drop in pH was noted in the 300-400 mm sample where the pH decreased from approximately 3.4 to less than 2.1 in 38 weeks (Figure 6.4a). The decrease in pH amongst the other control samples ranged from 0.8 to 1.2.

Whilst the application of lime at the $\frac{1}{2}$ pH-6 rate initially increased the pH of each tailings sample to at least 5.5, the pH of all tailings samples (with the notable exception of the 0-100 mm) dropped to levels comparable with the control treatment within 16 to 24 weeks of lime application (Figures 6.3 & 6.4). The application of lime at the 1 pH-6 rate similarly failed to maintain the pH of the tailings at circumneutral levels for the duration of the experiment. By week 48 the pH of all samples (again with the exception of the surface sample) had declined to levels approaching those of the control treatments (Figures 6.3 & 6.4).

Whilst the 2 pH-6 liming rate adequately maintained the pH of most of the treated tailings samples at levels greater than 6, the pH of tailings obtained from the 300-400 mm depth began to rapidly fall between weeks 24 and 32 of the experiment (Figure 6.4a). By week 76 of the experiment the average pH of this treatment had dropped almost 5 pH units to pH 2.03, a level lower than (but not significantly different from) that of the control treatment.

In contrast to the preceding liming rates, the 4 pH-6 and 8 pH-6 lime treatments were found to adequately maintain the pH of all amended tailings at levels in the vicinity of 7.5 for the duration of the experiment (Figures 6.3 & 6.4). At week 76 of the experiment there was no evidence to suggest that tailings treated with either of these rates of lime were beginning to reacidify.

An observation made during the course of the experiment that is not portrayed in Figures 6.3 & 6.4 was that while treatments were in a state of rapid pH decline, replicate samples often exhibited pH values that varied by more than 2 or 3 pH units. Without exception, however, the pH of the replicated samples were eventually found to reach an equilibrium pH very close to one another. To cite a specific example, at week 24 of the experiment, the 200-300 mm sample treated with lime at the 1 pH-6 rate was found to contain 2 replicate samples with pH values of 2.63 and 6.47. By week 48 of the experiment, however, these samples exhibited pH values of 1.84 and 1.85 respectively. Like most samples beyond week 48 of the experiment the tailings generally exhibited little further pH change. The non-synchronous pH decline observed between some replicate samples may have resulted from the uneven establishment of bacterial populations responsible for the catalytic oxidation of pyrite.

Graphs presented in Figures 6.3 & 6.4 show that where acidification of samples occurred, pH levels did not drop below about 2 regardless of the initial rate of pH decline or lime treatment. The buffering of sulphide bearing materials at similar pH levels has been reported in previous studies (Miller, 1979; Wiggering, 1993) and has been attributed to the dissolution of jarosite ($\text{KFe}_3(\text{OH})_6[\text{SO}_4]_2$), kaolinite and silica. Research indicates that even when sulphide-bearing materials are incubated in polyethylene bags under moist non-leaching conditions, rarely will pH levels fall below 1.5 (Dent, 1986). In acid-sulphate soils, acid hydrolysis of aluminosilicate clays is considered to be the primary pH buffering mechanism (Dent, 1986).

In colliery spoil, no strong buffering systems generally exist between pH 6.5 and 3.5, thus pH levels tend to drop very rapidly from circumneutral levels to strongly acid conditions upon exhaustion of acid neutralising carbonate minerals (Wiggering, 1993; Walder & Chavez, 1995). The Tui tailings are similarly considered to be devoid buffering systems within this pH zone and to be buffered at low pH chiefly by kaolinite and possibly jarosite and silica dissolution.

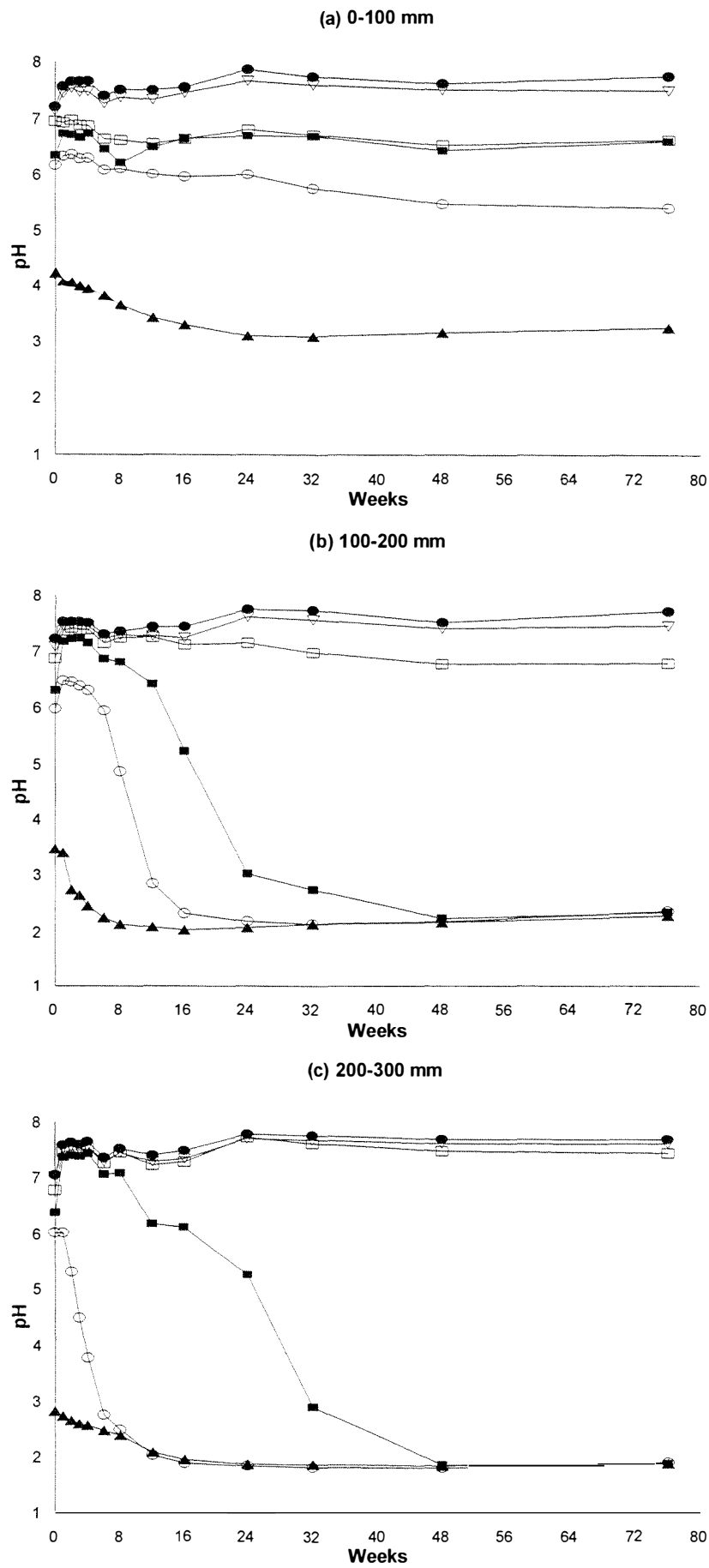


Figure 6.3 pH versus time in (a) 0-100 mm sample, (b) 100-200 mm sample and (c) 200-300 mm sample. Liming rates: nil (▲), half pH-6 (○), 1 pH-6 (■), 2 pH-6 (□), 4 pH-6 (▽) and 8 pH-6 (●).

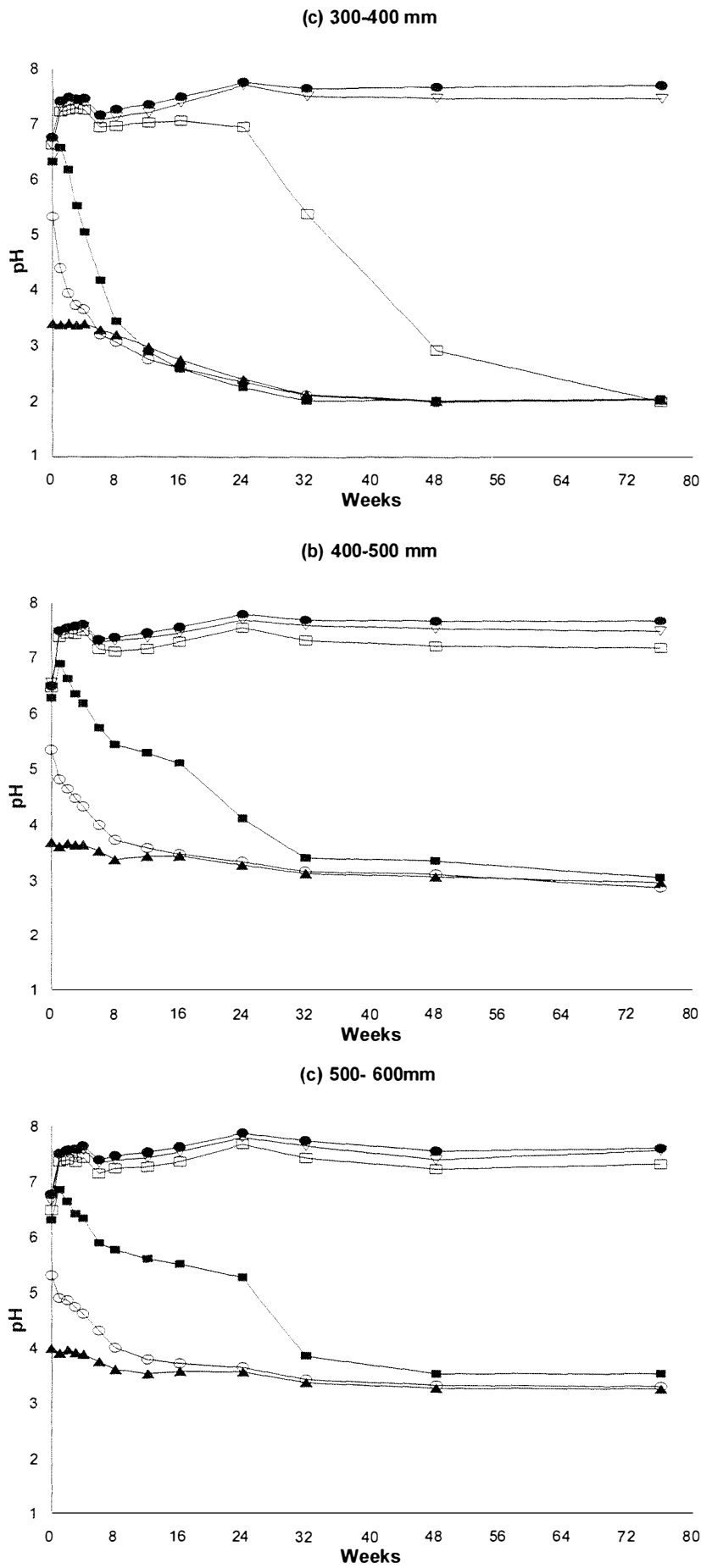


Figure 6.4 pH versus time in (a) 300-400 mm sample, (b) 400-500 mm sample and (c) 500-600 mm sample. Liming rates: nil (▲), half pH-6 (○), 1 pH-6 (■), 2 pH-6 (□), 4 pH-6 (▽) and 8 pH-6 (●).

6.4.1.2 Metal Concentrations

In contrast to sample pH, concentrations of 0.1M HCl extractable Cu, Fe and Zn were generally found to rise or remain relatively constant throughout the course of the experiment (Figures 6.5 to 6.10). The availability of these metals appears to have been related to both sampling depth and in some cases treatment. Metals were generally most readily available in samples below 200 mm depth and in tailings treated with the nil, ½ pH-6 or 1 pH-6 liming rates (Figures 6.5 to 6.12).

(i) Cu

In the case of Cu, the increase in the availability of this metal with time tended to be slightly higher in the control and ½ pH-6 lime treatments in samples obtained from the surface 300 mm of the profile (Figure 6.5). Tailings sampled from deeper in the profile, however, failed to demonstrate this same trend (Figure 6.6). One notable trend evident in Figures 6.6 b,c is the significantly lower concentrations of 0.1M HCl extractable Cu in the 8 pH-6 lime treated 400-600 mm zone tailings. The application of this relatively high rate of lime was found to reduce Cu levels from about 1000 mg/kg (or more) to less than 100 mg/kg in these samples (Figures 6.6 b,c). In contrast to the 8 pH-6 liming rate, the 2 and 4 pH-6 rates appeared to actually increase the amount of 0.1M HCl extractable Cu at corresponding depths.

It is postulated that the low availability of Cu in the 8 pH-6 treatments reflects the presence of excess, unreacted lime in the tailings which would have reduced the acidity of the 0.1M HCl extractant and therefore its ability to solubilise and extract Cu.

(ii) Fe

Like Cu, extractable Fe levels generally remained constant or increased during the course of the experiment depending upon treatment and depth (Figures 6.7 & 6.8). Whilst Fe levels in the uppermost sample (0-100 mm) remained relatively constant throughout the experiment regardless of treatment (Figure 6.7a), Fe levels in subsurface samples (100-600 mm) that received either ½, nil or 1 pH-6 lime rates were substantially higher at week 48 of the experiment than at week 0 (Figures 6.7 b,c & 6.8). The greatest 'liberation' of Fe occurred in the 200-300 mm sample where 0.1M HCl extractable Fe concentrations in the ½ pH-6 treatment increased by about 5000 mg/kg

during the course of the experiment (Figure 6.7c). At depths where relatively high levels of 0.1M HCl extractable Fe were initially present the effects of liming on Fe availability were immediately evident (Figures 6.8 a,b,c). Like Cu, levels of extractable Fe clearly tended to be much lower in those samples treated with the 8 pH-6 liming rate. In the 400-600 mm sampling zone the availability of Fe in the 2 pH-6 and 4 pH-6 treatments was also substantially lower (Figures 6.8 b,c). The 3 highest rates of lime were similarly appeared to prevent 0.1M HCl extractable Fe levels from appreciably increasing in the 100-200 and 200-300 mm samples during the course of the experiment (Figures 6.7 b,c).

(iii) Zn

In keeping with Cu and Fe, the levels of extractable Zn were low in the uppermost sample (0-100 mm) and remained relatively constant throughout the experiment regardless of treatment (Figure 6.9a). In most other samples, however, 0.1M HCl extractable Zn levels increased with time and were greatest in samples treated with either of the 3 lowest rates of lime (nil, $\frac{1}{2}$ pH-6, 1 pH-6). The difference between these rates is most readily observed in the sub-300 mm samples (Figures 6.10 a,b,c) where substantial increases in Zn are noted at week 48 of the experiment.

(iv) Pb

In contrast to 0.1M HCl extractable Cu, Fe and Zn concentrations, the availability of Pb in most treatments and at most depths declined with time (Figures 6.11 & 6.12). This trend is most readily observed in Figures 6.11 b in which Pb levels are seen to fall from about 1000 mg/kg at week 0 to between 100 and 400 mg/kg by week 32 of the experiment.

In most Pb plots it is apparent that where low quantities of lime were added to the tailings, available Pb levels were correspondingly low (Figures 6.11 & 6.12). This trend is readily seen in Figures 6.11 b and 6.12a and once again contrasts with trends generally observed for Cu, Fe and Zn (Figures 6.5 to 6.10).

Whilst the addition of lime at the 8 pH-6 rate seemed to increase the availability of Pb (relatively to other treatments) at most depths, within the 400-500 and 500-600 mm samples the addition of ^{lime} at this rate substantially reduced the extractability of Pb

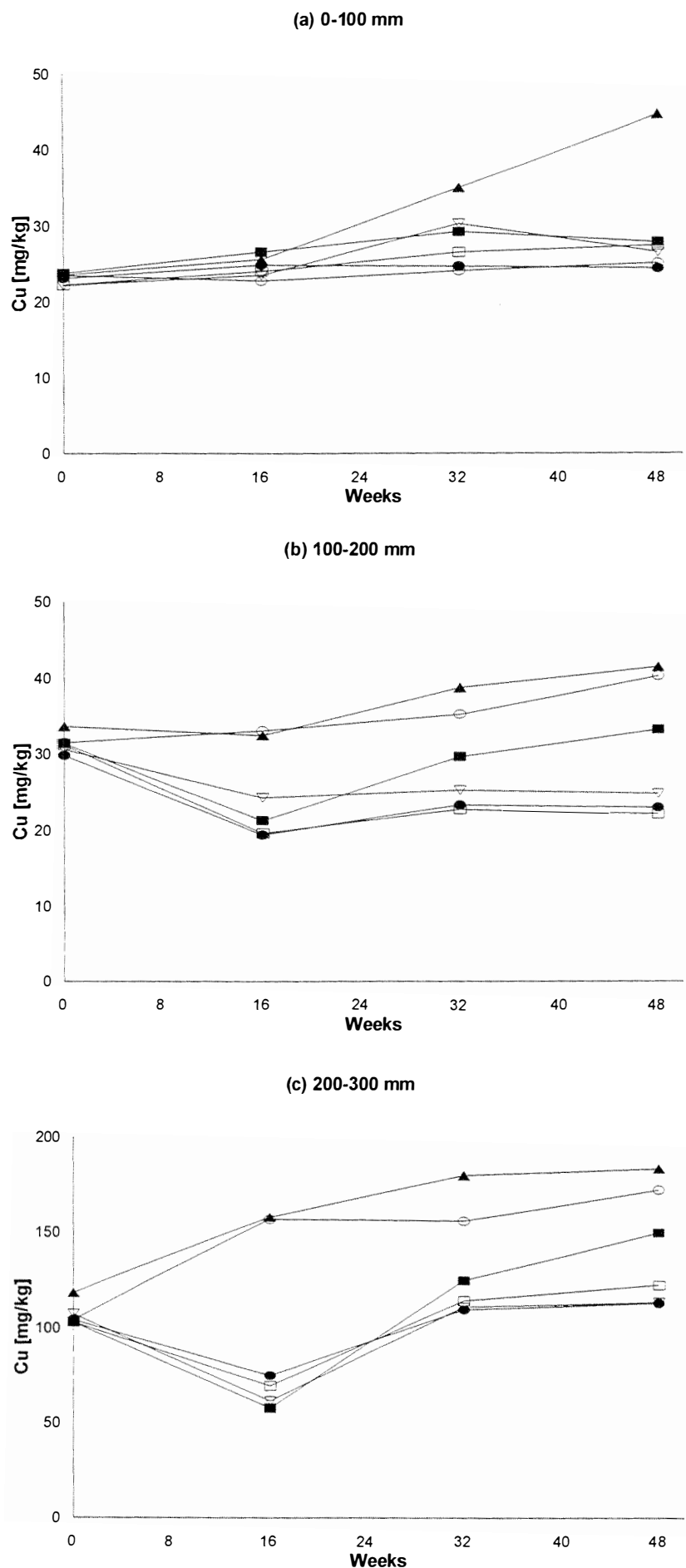


Figure 6.5 0.1M HCl extractable Cu versus time (a) 0-100 mm sample, (b) 100-200 mm sample and (c) 200-300 mm sample. Liming rates: nil (▲), half pH-6 (○), 1 pH-6 (■), 2 pH-6 (□), 4 pH-6 (▽) and 8 pH-6 (●).

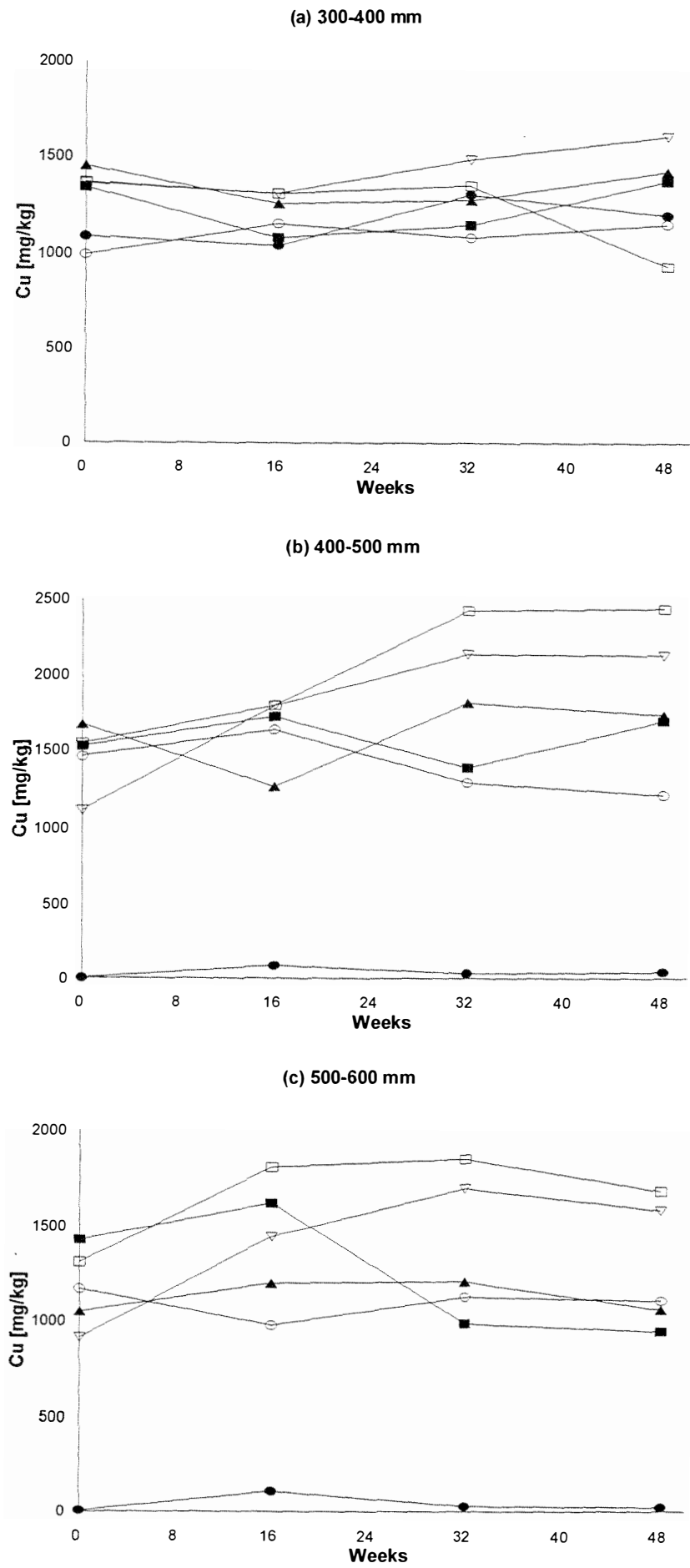


Figure 6.6 0.1M HCl extractable Cu versus time (a) 300-400 mm sample, (b) 400-500 mm sample and (c) 500-600 mm sample. Liming rates: nil (▲), half pH-6 (○), 1 pH-6 (■), 2 pH-6 (□), 4 pH-6 (▽) and 8 pH-6(●).

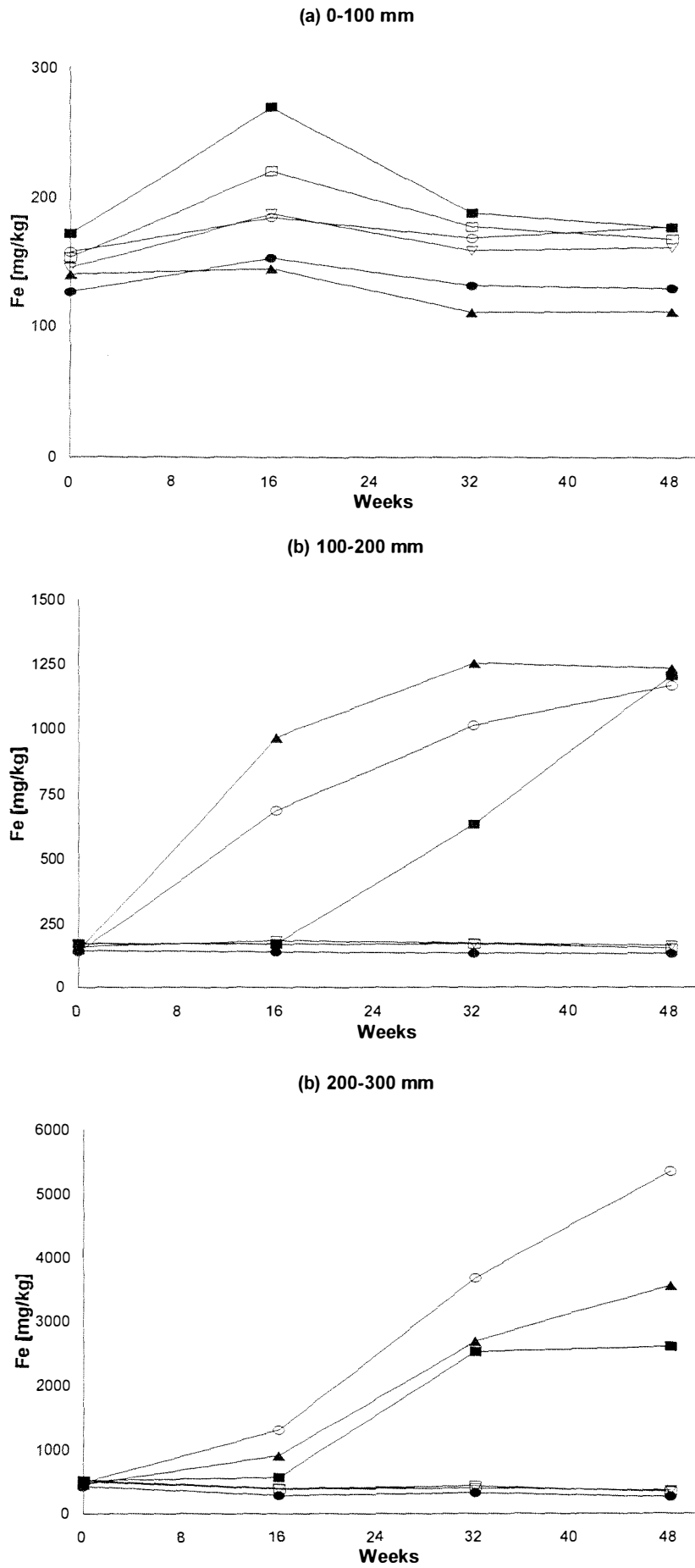


Figure 6.7 0.1 M HCl extractable Fe versus time (a) 0-100 mm sample, (b) 100-200 mm sample and (c) 200-300 mm sample. Liming rates: nil (▲), half pH-6 (○), 1 pH-6 (■), 2 pH-6 (□), 4 pH-6 (▽) and 8 pH-6 (●).

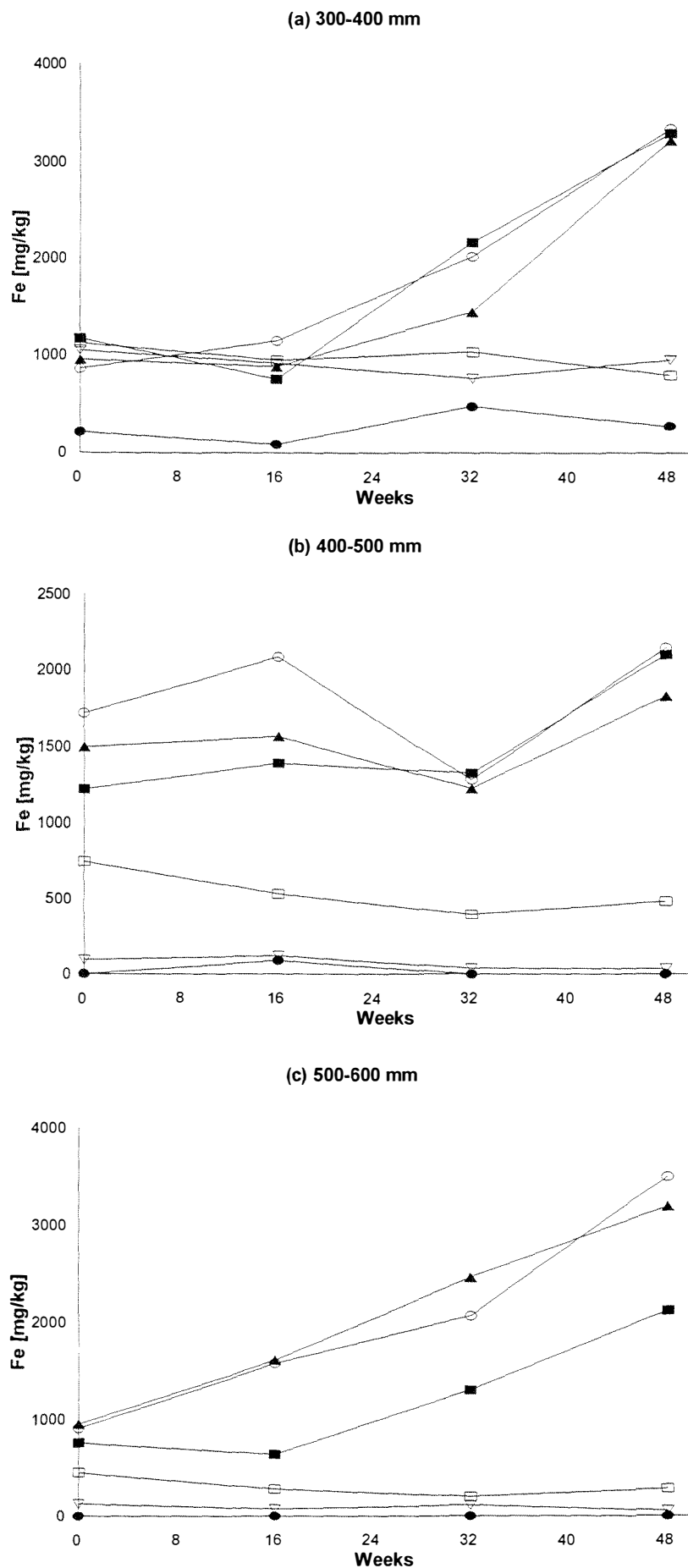


Figure 6.8 0.1M HCl extractable Fe versus time (a) 300-400 mm sample, (b) 400-500 mm sample and (c) 500-600 mm sample. Liming rates: nil (▲), half pH-6 (O), 1 pH-6 (■), 2 pH-6 (□), 4 pH-6 (▽) and 8 pH-6 (●).

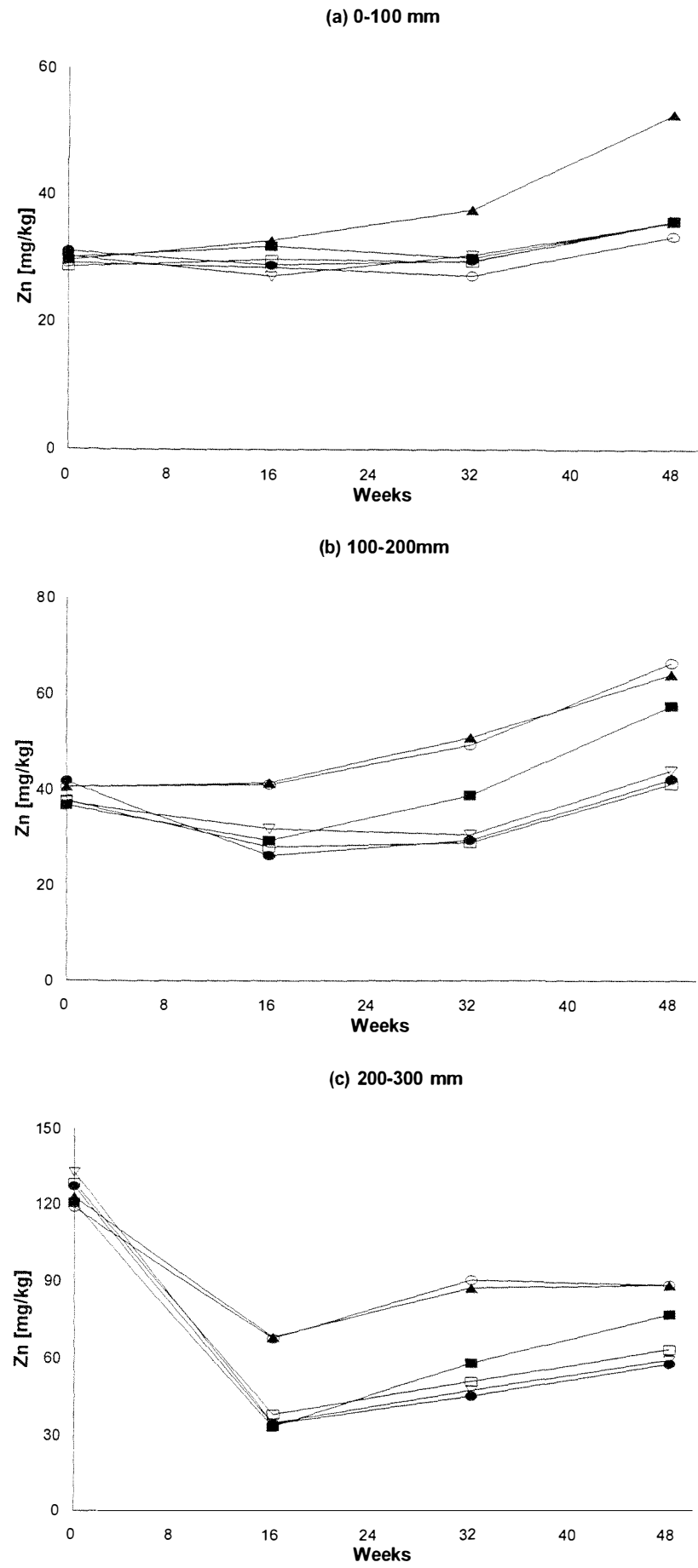


Figure 6.9 0.1M HCl extractable Zn versus time (a) 0-100 mm sample, (b) 100-200 mm sample and (c) 200-300 mm sample. Liming rates: nil (▲), half pH-6 (O), 1 pH-6 (■), 2 pH-6 (□), 4 pH-6 (▽) and 8 pH-6 (●).

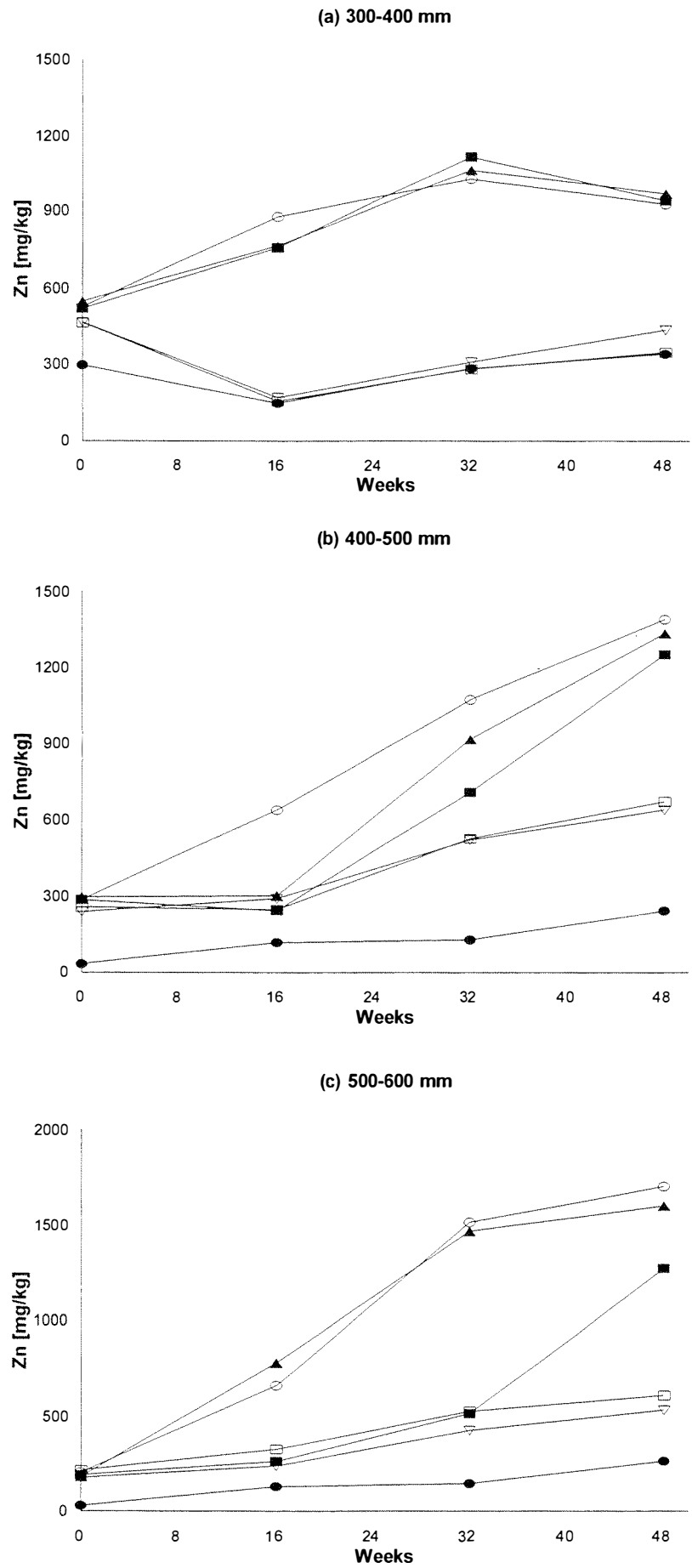


Figure 6.10 0.1M HCl extractable Zn versus time (a) 300-400 mm sample, (b) 400-500 mm sample and (c) 500-600 mm sample. Liming rates: nil (▲), half pH-6 (○), 1 pH-6 (■), 2 pH-6 (□), 4 pH-6 (▽) and 8 pH-6 (●).

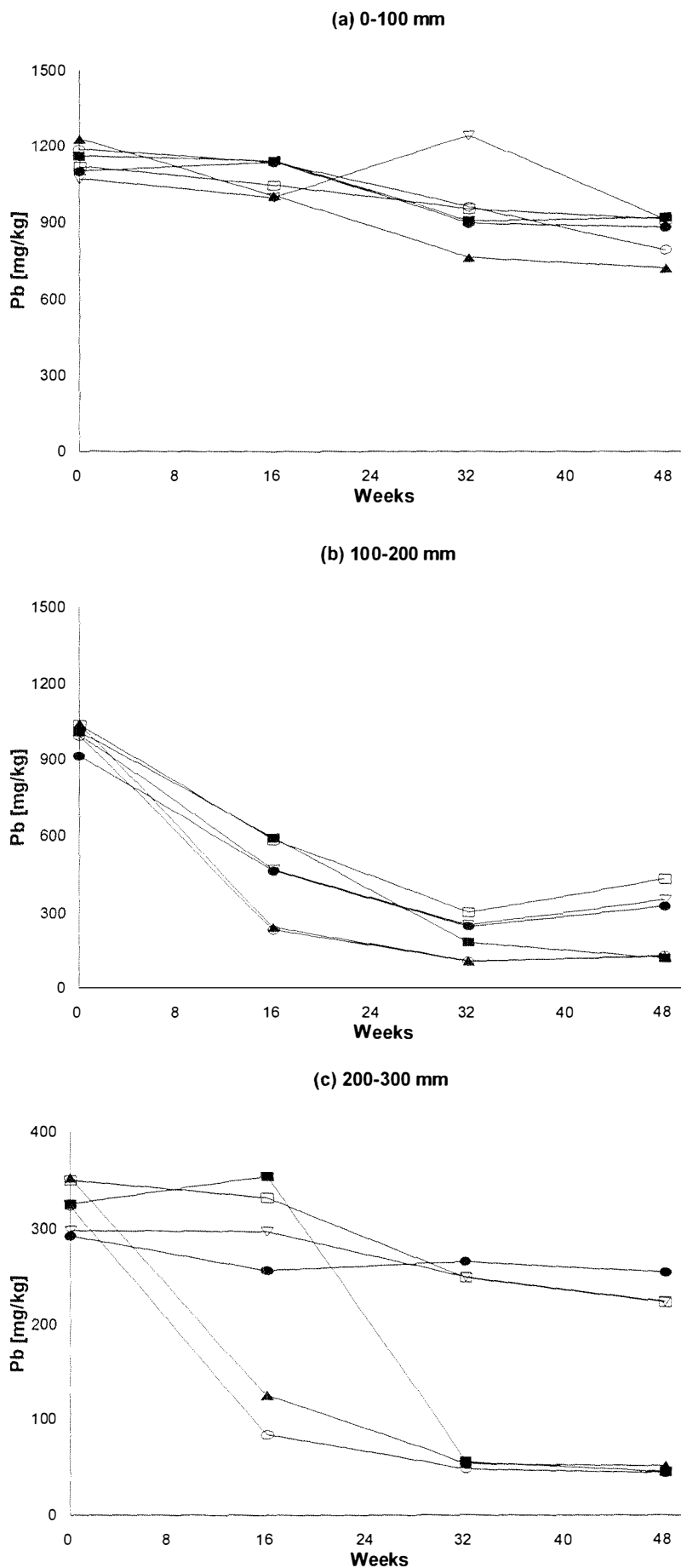


Figure 6.11 0.1M HCl extractable Pb versus time (a) 0-100 mm sample, (b) 100-200 mm sample and (c) 200-300 mm sample. Liming rates: nil (▲), half pH-6 (○), 1 pH-6 (■), 2 pH-6 (□), 4 pH-6 (▽) and 8 pH-6 (●).

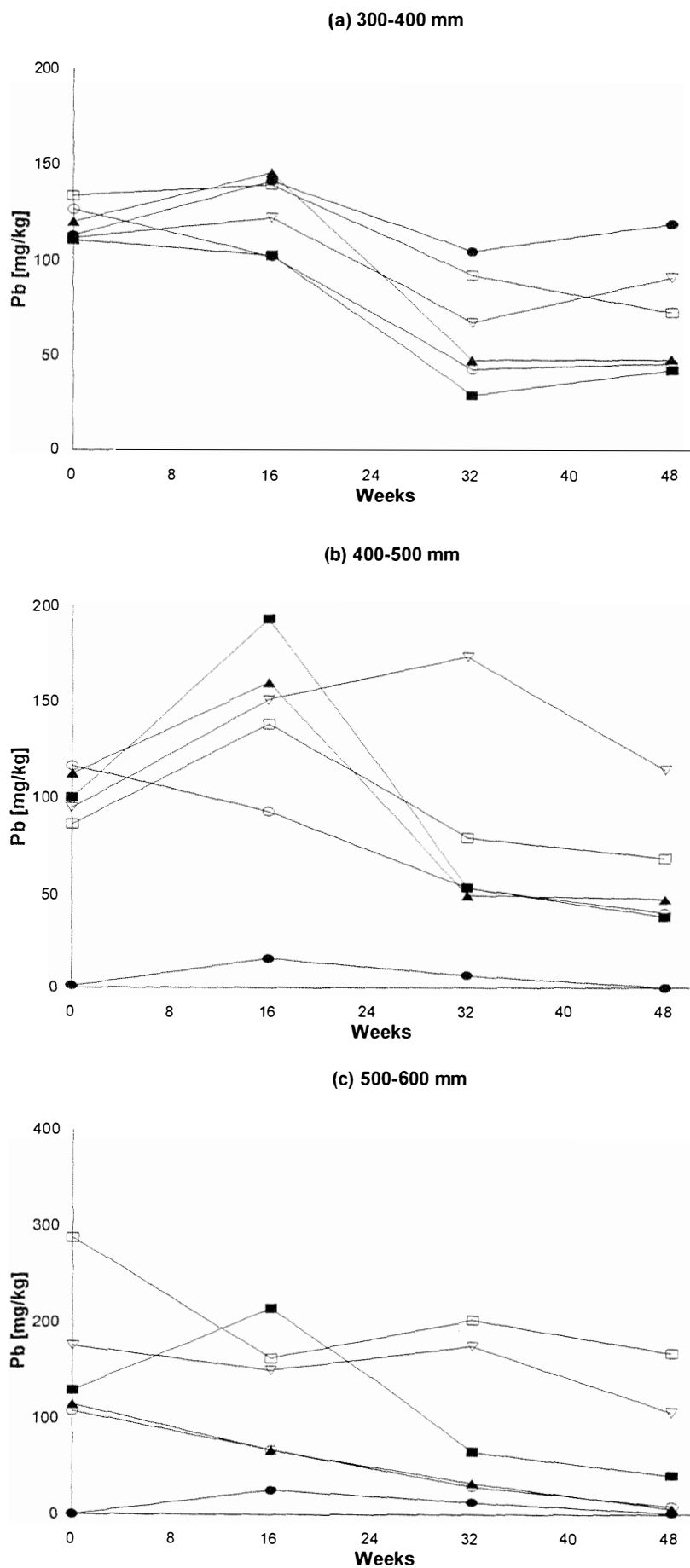


Figure 6.12 0.1M HCl extractable Pb versus time (a) 300-400 mm sample, (b) 400-500 mm sample and (c) 500-600 mm sample. Liming rates: nil (▲), half pH-6 (○), 1 pH-6 (■), 2 pH-6 (□), 4 pH-6 (▽) and 8 pH-6 (●).

(Figures 6.12 b,c). In this respect trends of Pb availability in the 400-600 mm zone were similar to those of Cu, Fe and Zn in 8 pH-6 treatments and may again have resulted from the extractant being effectively ‘neutralised’ due to the presence of excess lime and the precipitation of carbonates under highly alkaline conditions.

6.4.2 Variation in pH, Sulphate and Metal Levels with Depth and Liming Rate

The variation in pH and extractable metal concentrations with depth are most readily observed in Figures 6.13 to 6.16 which present parameter values versus depth on 4 separate occasions during the course of the experiment (weeks 0, 16, 32 & 48). Although as discussed in the previous section, treatment pH and extractable metal concentrations were in some samples highly time dependent, the overall trends with depth were consistent at most sampling times. The following discussion on the effects of lime and depth on pH and metal concentrations is based primarily on data (plots) presented in Figures 6.13 & 6.16 (weeks 0 and 48 of the experiment respectively) and upon ANOVA conducted on data presented in Figures 6.13 to 6.16.

6.4.2.1 pH

Figures 6.13e & 6.16e clearly indicate that pH levels were lowest in the 200-300 mm control sample. Tailings above and below this depth were consistently less acidic than this sample throughout the experiment. Whilst the addition of lime to the tailings was initially found to significantly increase the pH of tailings at each depth to levels in excess of pH 5, by week 48 of the experiment the effects of lime application at the $\frac{1}{2}$ pH-6 and 1 pH-6 rates were insignificant except in the surface sample (Figure 6.16e). By week 76 of the experiment the pH of the 300-400 mm tailings sample treated with the 2 pH-6 lime rate had similarly fallen to levels comparable with that of the control treatment (Figure 6.4a). Incremental samples treated with the 4 and 8 pH-6 liming rates, however, exhibited pH values that were consistently significantly higher than those of the nil, $\frac{1}{2}$ and 1 pH-6 treatments. Depth-wise pH variation was insignificant at the two highest liming rates.

ANOVA indicated that there was a significant interaction ($P < 0.001$) between liming rate and depth on pH and that the surface sample (0-100 mm) was most impacted by the addition of lime in terms of pH elevation. The mean pH of the surface sample was 6.12

at the end of the experiment. This compares with a mean pH of just 4.00 for the 300-400 mm sample which was least affected by lime addition. Interpretation of mean pH data indicates that the tailings obtained from the central region of the profile (between 100 and 400 mm depth) were most prone to reacidification.

Since ^{the}pH scale ^{is} logarithmic, it was recognised that the magnitude of pH change observed in various samples over time did not necessarily reflect the net release of acid due to oxidation. To elucidate the relative reactivity of the samples (in terms of the amount of acid (H^+) that they had generated) the antilogarithm of initial (week 0) and final (week 76) pH data (negative values) were taken to obtain H^+ concentrations. An estimate of the amount of H^+ generated by the samples during the course of the experiment was then estimated by subtracting the initial concentrations of H^+ from the final concentrations of H^+ . The estimated acidity produced by the tailings samples were then converted into units of calcium carbonate equivalence [$Mg\ CaCO_3/1000\ Mg\ of\ tailings$] as per the method outlined in Appendix 6(B).

It was recognised that the data generated using this method was only semi-quantitative in that it failed to quantify the effects of pH buffering by added lime and constituent minerals. In addition the method failed to account for the acidity potential generated by the hydrolysis of Fe^{3+} . Whilst titratable acidity would have provided a more accurate estimate of H^+ release, the method outlined in Appendix 6(B) was comparatively much faster and was considered to provide some indication of:- (i) the abilities of the comparative treatments to prevent reacidification and (ii) the depths at which the effects of sulphide oxidation were most prevalent.

The data presented in Figure 6.2b clearly indicates that the 200-300 mm sample was most reactive in terms of H^+ generation. Adjacent tailings samples (100-200 mm & 300-400 mm) were similarly found to liberate appreciable quantities of H^+ over the course of the experiment. In contrast, relatively small quantities of H^+ were liberated from the surface sample (0-100 mm) and from samples obtained from between 400-600 mm depth. Whilst the 'non-reactive' nature of the surface sample was consistent with Theoretical Acid Generating Potential (TAGP) trends presented in Figure 6.2a, the low

rate of acid generation in the 400-600 mm zone was unexpected and clearly contradictory to predicted TAGP results.

In the field the less reactive nature of tailings samples at lower depths would be readily explained by their comparatively poor aeration and the presumed low activity of aerobic, iron-oxidising bacteria (Sorensen *et al.*, 1980). Although no attempt was made to monitor the establishment of *Thiobacilli* spp. in the various samples, the conditions used for the incubation were considered to be conducive to their establishment and thus for both biotic and abiotic sulphide oxidation to take place. The apparent anomaly between predicted acid generation (ie. TAGP) and observed acid generation (ie. H^+ liberation) is therefore, attributed to grain size variation within the tailings profile and hence between incremental tailings samples. Whilst pyrite activity is dependent on a number of variables⁵ it is widely accepted that one of the most important factors governing its reactivity is the amount of exposed surface area which is in turn a function of grain size (Caruccio, 1973; Pugh *et al.*, 1984; Burt & Caruccio, 1986; Caruccio *et al.*, 1988). Grainsize analysis indicated that tailings sampled from between 200-400 mm depth contained appreciably higher amounts of silt-sized particles than tailings obtained from other depths (Figure 6.17a). Regression analysis confirmed that there was a positive ($P < 0.1$) correlation between the quantity of silt-sized particles in the samples and H^+ generation (Figure 6.17b).

Whilst grain size variation does not explain the difference in reactivity between the 100-200 mm and 400-500 mm sample, it is postulated that populations of *Thiobacillus* spp. responsible for the accelerating the generation of Fe^{3+} (and therefore sulphide oxidation) would have been better established in the upper sample at the time of sampling due to its closer *in situ* proximity to the surface of the tailings and hence atmospheric oxygen.

ANOVA indicated that mean H^+ levels were significantly higher in samples treated with the nil, $\frac{1}{2}$ pH-6 and 1 pH-6 liming rates. This finding is important in that it indicates that the application of lime at rates < 1 pH-6 were ineffective at preventing H^+ generation. Similarly at the 300-400 mm depth, significant quantities of H^+ were generated in tailings treated with lime at the 2 pH-6 rate (Figure 6.2b). In contrast to the aforementioned treatments, acid generation values obtained for the 4 and 8 pH-6

treatments were negative, indicating that mean H^+ concentrations in fact diminished in these treatments during the course of the experiment. The slight increase in pH and hence the ‘consumption’ of H^+ is presumed to reflect the dissolution of $CaCO_3$ in the admixes as they continued to equilibrate with time. Many poorly buffered materials will exhibit pH of about 8.4 if they contain free $CaCO_3$ and water, the equilibrium pH for a saturated solution of $CaCO_3$ in the presence of atmospheric CO_2 (Walder & Chavez, 1995).

The results obtained for the 4 pH-6 and 8 pH-6 treatments indicate that either:- (1) acid was generated and then neutralised by the applied lime, or alternatively that (2) negligible oxidation occurred in these samples. Based on previous research reported in Chapter 3 (section 3.6.3), it is postulated that very little oxidation would have occurred in these heavily limed treatments. Alkaline conditions are generally accepted to severely inhibit sulphide oxidation by precipitating the primary sulphide oxidising agent (Fe^{3+}) and by creating conditions poorly suited to the activity of acidophilic, iron-oxidising bacteria which generate this oxidant (Chapter 3; sections 3.3.1 & 3.6.3).

6.4.2.2 Metal Concentrations

The concentrations of 0.1M HCl extractable Cu, Fe and Zn showed largely similar trends over the duration of the experiment with depth (Figures 6.13 to 6.16). Levels were almost without exception lowest and least variable in the surface 300 mm of the profile. The effects of liming were negligible in these samples throughout most of the experiment, although by week 16 significant differences in Fe concentrations had developed between some limed treatments (Figure 6.16b). In sub-300 mm depth samples the concentrations of these metals increased substantially and significant differences in extractable metal concentrations were apparent between most lime treatments (Figures 6.13 to 6.16).

(i) Cu

In the case of Cu, 0.1M HCl extractable levels were comparable in sub-300 mm samples with the exception of the 400-500 mm and 500-600 mm samples treated with the 8 pH-6 lime rate. Extractable Cu levels in these treatments were negligible (Figures 6.13 to

⁵ See Chapter 3 (section 3.3.3) for discussion.

6.16). At week 48 of the experiment ANOVA indicated that there remained a significant interaction between liming rate and depth and that mean Cu levels were greatest in the 400-500 mm samples (1542 mg/kg) and least in ^{the} two surface samples (c. 30 mg/kg). The 8 pH-6 liming rate was found to be most effective at reducing the availability of the Cu and the 2 and 4 pH-6 treatments least effective.

(ii) Fe

Whereas no distinct trends were evident amongst liming rates for Cu samples, Fe levels clearly tended to be highest in the nil, $\frac{1}{2}$ and 1 pH-6 treatments throughout the experiment (potential mechanisms are discussed in section 6.4.4). Whilst mean Fe levels extracted from these treatments were not significantly different at week 0, by week 16 of the experiment significantly greater mean concentrations of Fe were extracted from the $\frac{1}{2}$ pH-6 treatments than from the control treatment (Figure 6.16b). The 4 and 8 pH-6 liming rates were found to be most effective at reducing the availability of Fe in the samples. Levels in these treatments were reduced to about 10% or less of those found in the $\frac{1}{2}$ pH-6 treatments. ANOVA indicated that mean Fe concentrations were significantly higher in the 200-400 mm depth zone (c.2000 mg/kg) and lowest in the surface tailings (154 mg/kg) (Figure 6.16b).

(iii) Zn

Zinc levels, like Fe concentrations, were similarly found to increase significantly below 300 mm depth, particularly in the treatments receiving lime at rates of 1 pH-6 or less (Figures 6.13 to 6.16). Although mean levels of 0.1M HCl extractable Zn tended to be greatest in the 300-400 mm samples in the initial stages of the experiment (ie. up until at least week 16) greater concentrations were detected in the 500-600 mm sample at and beyond week 32. Although ANOVA indicated that mean Zn concentrations were significantly higher in the $\frac{1}{2}$ pH-6 lime treatments than in the control at week 16, the differences were insignificant at weeks 0, 32 and 48 of the experiment.

(iv) Pb

Lead exhibited a contrasting trend with depth to Cu, Fe and Zn. As opposed to increasing with depth, levels of 0.1M HCl extractable Pb were found to decrease with depth (Figures 6.13 to 6.16). The most significant decrease in Pb was found to occur

between the 100-200 mm and 200-300 mm samples, where concentrations decreased by about 500 mg/kg.

Although Pb concentrations were not greatly affected by liming rates, ANOVA of week 48 data indicates that mean Pb levels were lowest in those samples that received either the nil or $\frac{1}{2}$ pH-6 rate of lime. Differences in mean extractable Pb concentrations between these treatments were negligible (6.16 b). With the exception of week zero data, 0.1M HCl extractable Pb levels were consistently higher in the 2, 4 & 8 pH-6 lime treated tailings; a finding that clearly differs from trends observed with Cu, Fe and Zn (see discussion in section 6.4.3).

The decrease in 0.1M HCl extractable Pb with depth is consistent with findings reported in Chapter 5 which indicate that PbSO_4 (anglesite) concentrations are appreciably higher near the surface of the tailings and decrease with depth.

(v) Sulphate

Sulphate levels as analysed on week 16 of the experiment were found to generally increase with depth. Mean 0.1M HCl extractable $\text{SO}_4^{=}$ levels were approximately 10 times lower in the surface sample than in the 500-600 mm sample (Figure 6.14f). ANOVA indicated that similarly to Fe, higher mean levels of $\text{SO}_4^{=}$ were extracted from the $\frac{1}{2}$ pH-6 lime (2106 mg/kg) treatment than from the control treatment (1620 mg/kg). As the liming rate was increased above this rate, however, extractable $\text{SO}_4^{=}$ levels decreased.

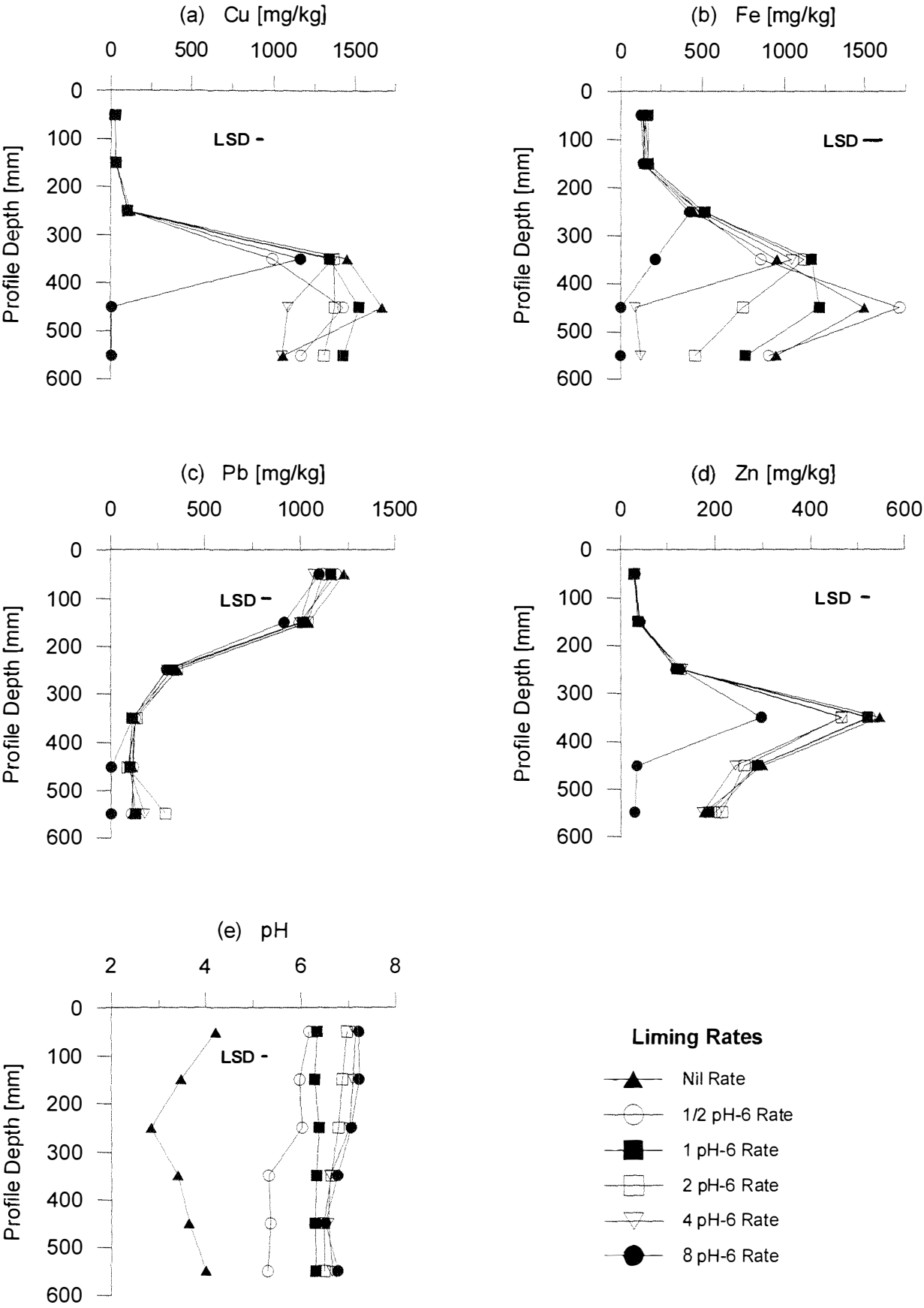


Figure 6.13 Variation of pH and 0.1M HCl extractable metal concentrations with depth and liming rate at week zero. LSD = Depth/Rate Interaction (5%)

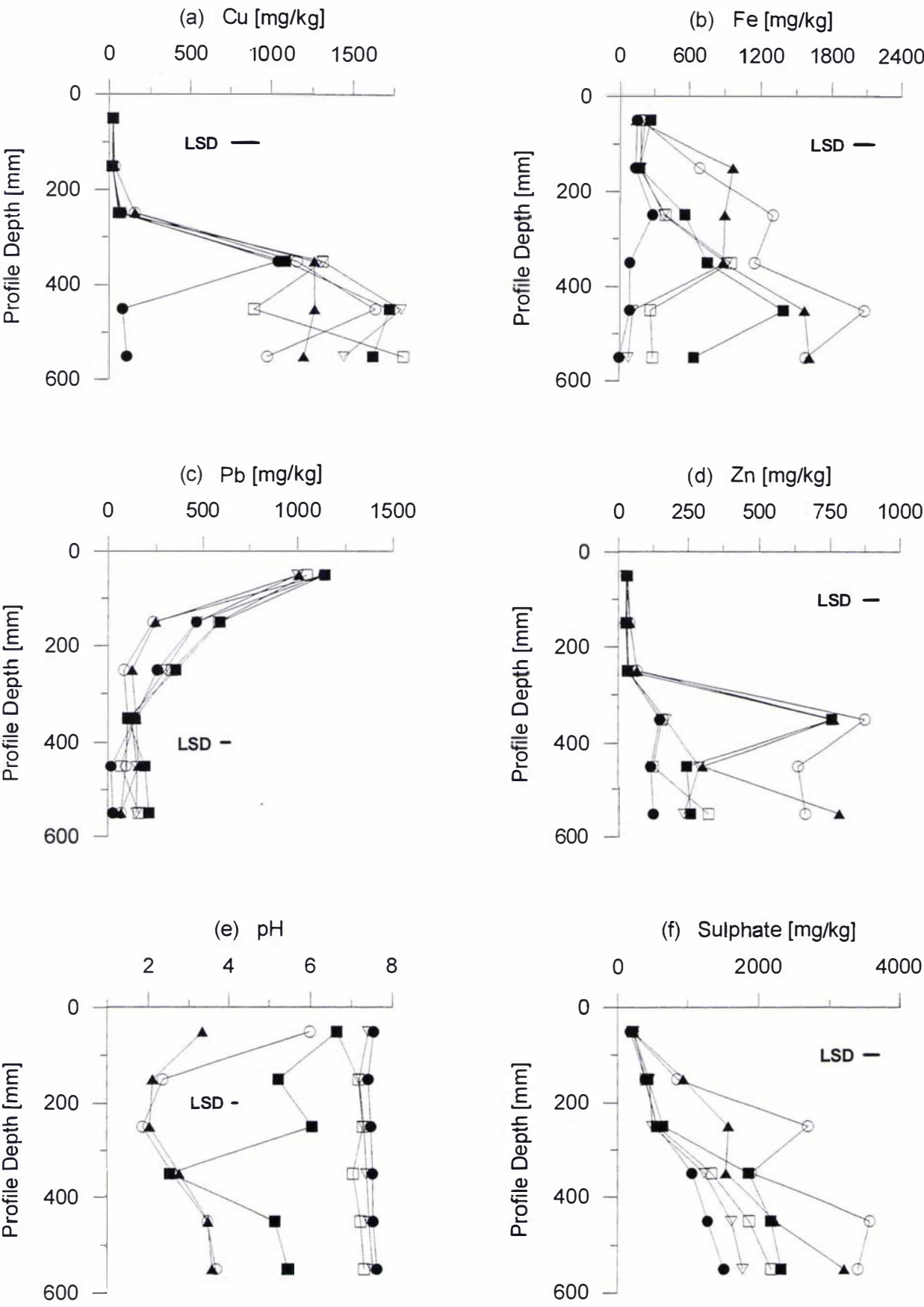


Figure 6.14 Variation of pH and 0.1M HCl extractable sulphate and metal concentrations with depth and liming rate at week 16. LSD = Depth/Rate Interaction (5%)

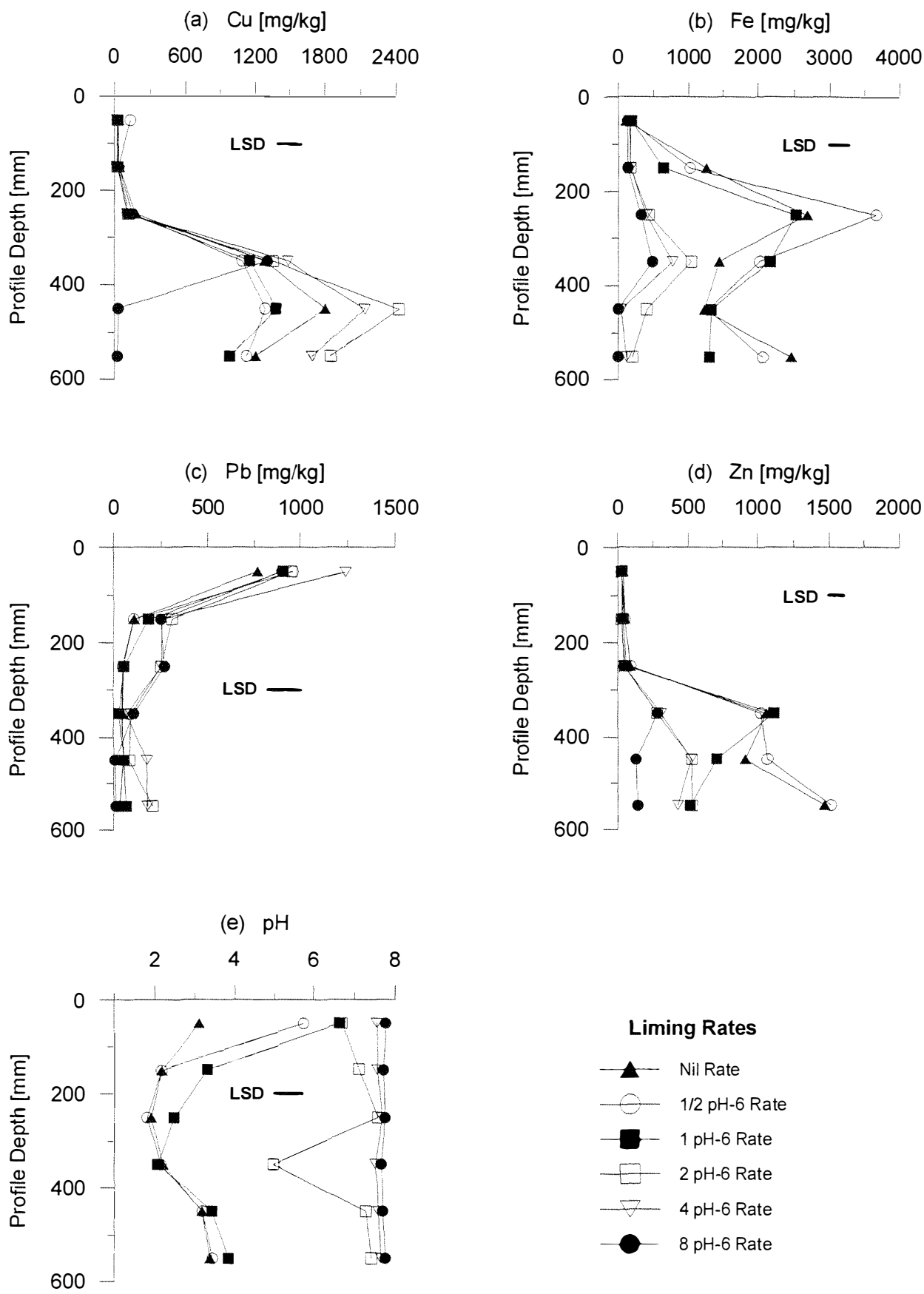


Figure 6.15 Variation of pH and 0.1M HCl extractable metal concentrations with depth and liming rate at week 32. LSD = Depth/Rate Interaction (5%)

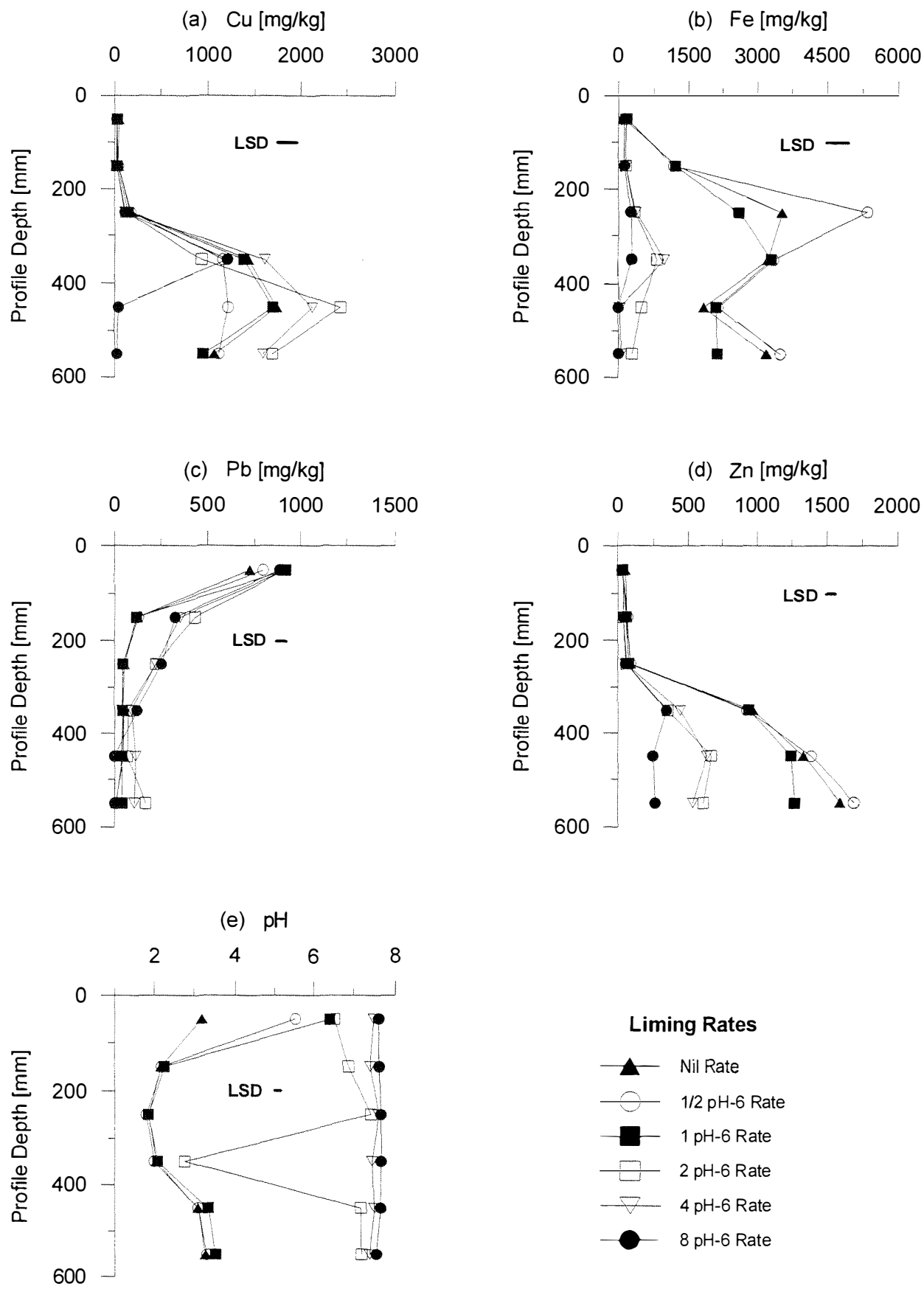


Figure 6.16 Variation of pH and 0.1M HCl extractable metal concentrations with depth and liming rate at week 48. LSD = Depth/Rate Interaction (5%)

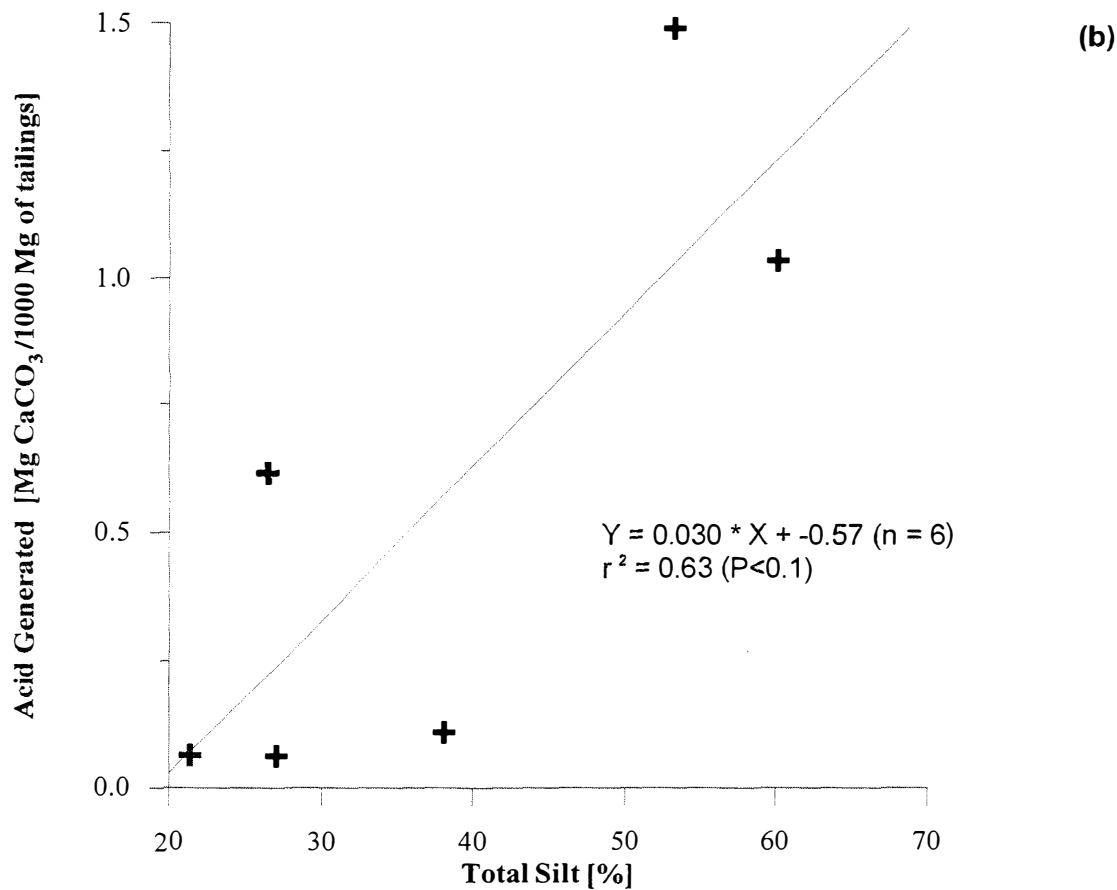
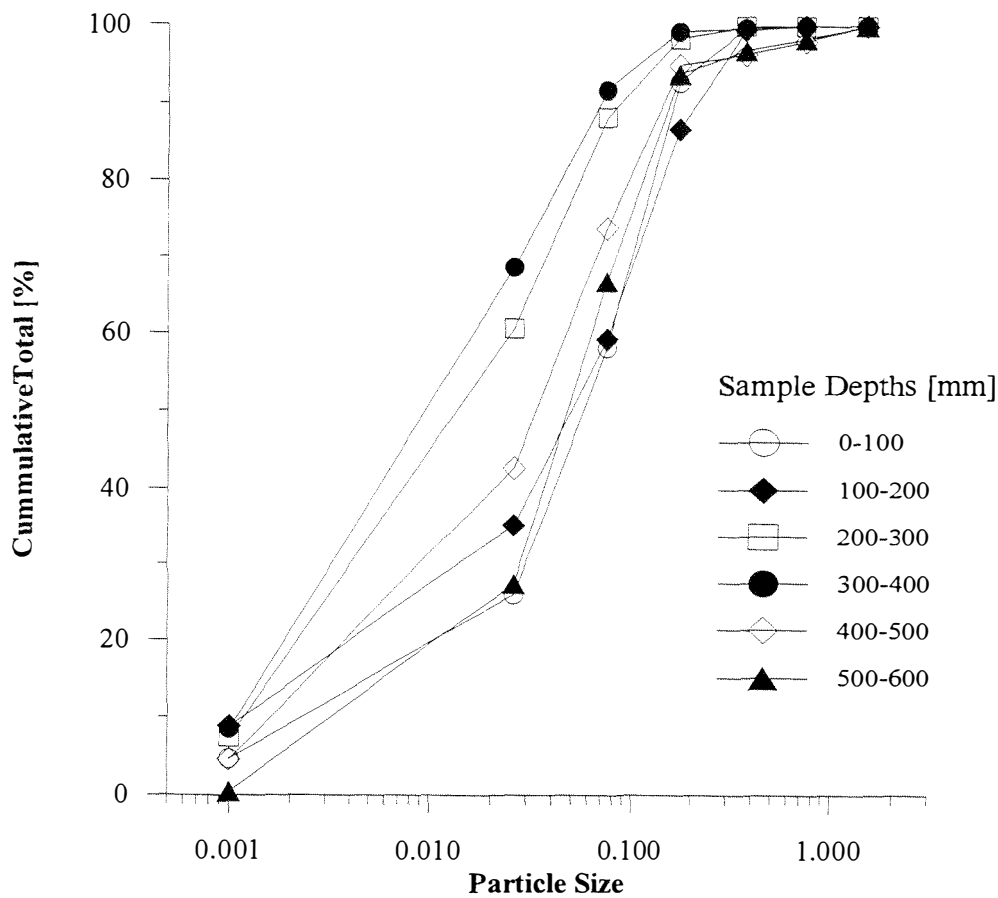


Figure 6.17 (a) Cumulative percent versus particle size of the incremental tailings samples obtained from grid sampling site 7. **(b)** Correlation of hydrogen ion liberation from control treatment samples versus the silt content of the samples.

6.4.3 Parameter Correlation Analysis

To elucidate the interaction of the various measured parameters, correlation analysis was conducted on the combined data from each of the 4 sampling times (Table 6.5). With the exception of Cu versus pH, correlation coefficients between the various parameters were found to be either highly significant ($P < 0.01$) or very highly significant ($P < 0.001$).

The data presented in Table 6.5 indicates that whereas Cu, Fe, Zn and $\text{SO}_4^{=}$ were negatively correlated to pH, Pb was positively correlated. The increase in the availability of Cu, Fe and Zn at low pH is readily explained by the well known relationship between pH and heavy metal availability⁶ (Alloway, 1995). It is generally observed that in the absence of high CEC clays and organic matter heavy metals cations are most mobile and thus most readily extracted under acid conditions.

The solubility of metal species is not only dependent on pH but is also governed by a variety of other environmental parameters including the relative quantities of potential complexing anions such as $\text{SO}_4^{=}$ and $\text{CO}_3^{=}$ in solution (Ritcey, 1989; Alloway, 1995). Clearly in the case of Pb, the geochemical conditions prevailing in the incubated tailings samples were immobilising Pb, particularly in those treatments that received little or no lime. Thermodynamic data indicates that in acidic ($\text{pH} < 5.5$) oxidising conditions dissolved Pb species tend to form highly insoluble anglesite (PbSO_4) with $\text{SO}_4^{=}$ (Brookins, 1988). As the pH increases above 5.5, however, the formation of cerussite (PbCO_3) is promoted especially in the presence of lime (CaCO_3). The dissolution of PbCO_3 may explain the small but significantly higher mean concentrations of Pb extracted from the 1, 2, 4 and 8 pH-6 treatments.

The overall trends observed in Figures 6.11 & 6.12 which show that 0.1M HCl extractable Pb concentrations generally decreased with time. It is postulated that the overall incubation process was conducive to the formation of highly insoluble PbSO_4 and that liberation of $\text{SO}_4^{=}$ during the course of the experiment effectively enhanced PbSO_4 formation. The production of $\text{SO}_4^{=}$ is believed to reduce the solubility of sulphate minerals such as anglesite by increasing the activity of $\text{SO}_4^{=}$ (Walder &

⁶ The high availability of most metals at low pH results from the combined effects of high metal solubility and the decrease in the negative surface charge of colloids capable of complexing metal cations.

Chavez, 1995). The strong negative correlation between extractable Pb and $\text{SO}_4^{=}$ identified in the present study clearly indicates that in the presence of high $\text{SO}_4^{=}$ concentrations Pb levels were conversely low (Figure 6.18b). Decreasing pH during the course of the experiment would have similarly promoted the formation of anglesite and therefore further reduced extractable Pb concentrations.

Table 6.5 Significance of Pearson’s Correlation Coefficient (bracketed data) of measured parameters. PS = possibly significant ($P<0.1$); S = significant ($P<0.05$); S* = highly significant ($P<0.01$); S** = very highly significant ($P<0.001$). Degrees of freedom = 142 for Cu, Fe, Pb and Zn and 34 for $\text{SO}_4^{=}$.

	pH	Cu	Fe	Pb	Zn	$\text{SO}_4^{=}$
pH	1					
Cu	PS (-0.189)	1				
Fe	S** (-0.707)	S** (0.415)	1			
Pb	S* (0.283)	S** (-0.631)	S** (-0.461)	1		
Zn	S* (-0.308)	S** (0.892)	S** (0.493)	S** (-0.674)	1	
$\text{SO}_4^{=}$	S* (-0.440)	S** (0.797)	S** (0.774)	S** (-0.706)	S** (0.849)	1

In contrast to Pb, Fe concentrations were positively correlated to $\text{SO}_4^{=}$ levels in the tailings samples (Figure 6.18a). This relationship is consistent with the process of sulphide oxidation that as described in Chapter 3 (section 3.3) which results in the formation of $\text{SO}_4^{=}$, Fe^{2+} and acidity (Backes *et al.*, 1986). Correlation of Fe and $\text{SO}_4^{=}$ versus pH showed similar negative correlation which indicates that at low pH these species were more generally more readily available (Table 6.5).

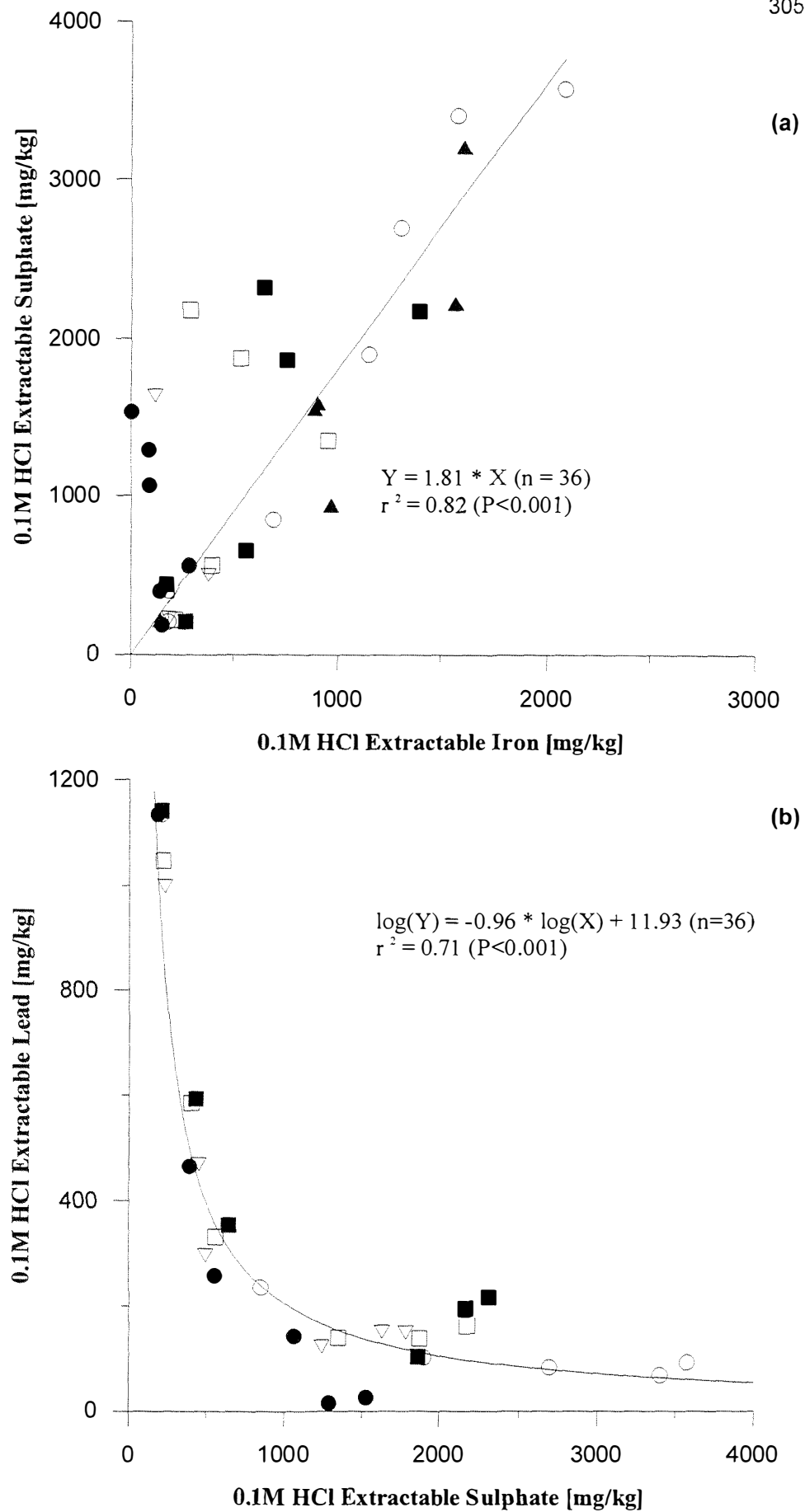


Figure 6.18 (a) Correlation of 0.1M HCl extractable sulphate versus iron at week 16.
(b) Correlation of 0.1M HCl extractable lead versus sulphate at week 16.

6.4.4 Discussion of Results

Results presented in sections 6.34 and 6.42 provide evidence that suggests that the treatment of Tui tailings with lime at the $\frac{1}{2}$ pH-6 rate have enhanced sulphide oxidation in incubated samples (Figures 6.14 to 6.16). ANOVA indicated that mean concentrations of 0.1M HCl extractable Fe and $\text{SO}_4^{=}$ were significantly higher in the $\frac{1}{2}$ pH-6 treatment than in the non-limed tailings (ie. control treatments). The 'positive' effect of lime on Fe levels were most marked in the 200-300 mm depth samples at and beyond week 16 of the experiment (Figures 6.14b to 6.16b). A high sulphate level was also observed in this treatment at week 16 of the experiment (Figure 6.14f).

The tailings depth of maximum Fe availability (200-300 mm) was found to coincide with the depth at which maximum H^+ generation occurred (Figure 6.2b). Although this observation may simply reflect the greater mobility of Fe under acidic conditions, it may alternatively indicate that the tailings in this zone were highly reactive and more susceptible to oxidation than tailings originating from other depths.

Whilst it is widely accepted that the addition of neutralising agents such as CaCO_3 generally inhibit the process of sulphide oxidation⁷ (Geidel, 1979; Caruccio *et al.*, 1984; Walder & Chavez, 1995), other studies indicate that relatively low rates of lime application may in fact accelerate the rate of abiotic sulphide oxidation (Backes *et al.*, 1986; Burt & Caruccio, 1986). In a study which was designed to investigate the effects of limestone treatment on pyritic waste-rock⁸ Burt & Caruccio (1979) found that solutions containing dissolved limestone consistently accelerated the rate of pyrite oxidation when applied at concentrations below a critical alkalinity threshold value. High rates of oxidation were also initially observed in admixes of solid limestone and waste-rock.

⁷ It is generally believed that the inhibition of sulphide oxidation as a result of lime application is associated with the creation of circumneutral or alkaline pH conditions which are effectively hostile to the growth of *Thiobacillus* spp. (Chapter 3, section 3.6.3).

⁸ The waste rock originated from the Haile Gold Mine in South Carolina, USA.

The mechanism proposed by Burt & Caruccio (1986) to explain the accelerated oxidation rates is that at circumneutral pH the abiotic oxidation rate of Fe^{2+} to Fe^{3+} is far greater⁹ than it is under strongly acidic pH conditions. This, they suggested, results in the higher concentrations of Fe^{3+} at the pyrite surface which in turn increases oxidation. Providing the alkalinity is maintained above a certain threshold alkalinity value, Burt & Caruccio (1986) proposed that the precipitation of Fe^{3+} via the formation of hydrous iron oxides at the pyrite surface outpaces acid generation and coats the pyrite surface reducing the rate of oxidation. In the case where insufficient alkalinity is present within the 'soil solution' to precipitate substantial amounts of Fe^{3+} , however, the oxidation rate of the pyrite may be accelerated until strong acid conditions re-establish. This mechanism may be further enhanced by the preservation of very acidic microenvironmental conditions at the surface of the sulphide mineral.

Whilst the mechanism proposed by Burt & Caruccio (1986) provides a potential explanation for the trends observed in the present lime incubation experiment, it must be stressed that the earlier leaching experiments conducted by Burt & Caruccio (1986) were conducted under abiotic conditions and thus neglected to consider the influence of iron-oxidising bacteria. As previously mentioned in this chapter, acidophilic bacteria are considered to play an extremely important role in the oxidation of pyrite (and other sulphides) because they catalyse and accelerate the rate of Fe^{2+} oxidation at low pH (ie. <3.5). Their presence is important to the overall rate of pyrite oxidation in that they effectively provide a ready source of Fe^{3+} in acidic conditions. Fe^{3+} iron is only appreciably soluble in solutions below pH 3.5. Its solubility dramatically decreases as pH increases to the extent whereby at pH 5.5 almost all Fe^{3+} is precipitated as hydrous ferric oxides (Brookins, 1988; Walder & Chavez, 1995).

Considering that the present experiment was conducted under conditions that were believed to be favourable for the growth of *Thiobacillus* spp. (Ahonen & Tuovinen, 1991; Okereke & Stevens, 1991) direct comparison between the results of this study and that of Burt & Caruccio (1986) may be imprudent. It is possible, however, that the aforementioned mechanism may still explain the inferred results of the present study

⁹ Research cited in Burt & Caruccio (1986) indicates that under abiotic conditions the oxidation of Fe^{2+} to Fe^{3+} occurs at rates 5 orders of magnitude greater at pH 7 than at pH 3.

despite the presumed presence of iron-oxidising bacteria in the tailings. It is postulated that the effects of liming in terms of enhancing abiotic Fe^{2+} oxidation may have outweighed the inhibitory effect of lime (pH) on bacterial activity. Whilst the augmentation of pH above 3 is generally considered^{to} inhibit *Thiobacillus ferrooxidans*¹⁰ most strains of this bacteria are tolerant of pH levels of up to 5.2 (Smith 1974; Ritcey, 1989). Although the pH of the ½ pH-6 treated tailings initially reached levels in excess of 5 much lower pH levels were probably maintained at the mineral surface which would have provided an environment sufficiently acidic to facilitate the activity of acidophilic bacteria.

A second mechanism that could have initially bolstered the oxidation process is also proposed:- (1) initial (temporary) pH increase afforded by ½ pH-6 liming rate resulted in the rapid abiotic oxidation of Fe^{2+} to Fe^{3+} , (2) falling pH then remobilised Fe^{3+} and facilitated its involvement in pyrite oxidation.

6.5 Chapter 6 Summary & Conclusions

- The lime incubation experiment confirmed that the surface tailings (0-200 mm tailings) have been extensively oxidised and have little capacity to generate acidity and to liberate metals. Contrary to predicted TAGP results tailings obtained from the 500-600 mm depth zone did not appear to be the most reactive in terms of generating acidity.
- The results are interpreted as indicating that the tailings in the 200-400 mm zone were more prone to oxidation. This finding is believed to reflect variations in the mean grain size of the tailings and hence in the effective surface area of acid generating sulphide minerals exposed.
- This experiment also clearly demonstrated that the use of simple pH buffering techniques to predict the liming requirement of materials are poorly suited to materials containing reactive sulphide minerals exposed to oxidising conditions. Most tailings samples limed to pH 6 were found to rapidly reacidify to levels well below that suited to the establishment and growth of plants.

¹⁰ Although *T. ferrooxidans* is considered to be the most important organism associated with pyrite oxidation over a dozen species of bacteria may potentially be involved (Ritcey, 1989).

- The 4 pH-6 liming rate was identified as being sufficiently high to prevent reacidification of all tailings samples over a 1½ year period. Despite some temporal and spatial variation, the 8 pH-6 liming rate was generally found to be the most successful treatment for immobilising Cu, Fe and Zn. This finding is believed to at least in part reflect the ability of high liming rates to effectively neutralise the acid extractant used.
- This experiment confirmed results presented in Chapter 4 that indicated that 0.1M HCl extractable Pb concentrations are very high in the tailings, particularly near the surface of the profile (0-200 mm). In contrast, concentrations of Cu, Fe and Zn were lowest in this region of the profile. These findings again reflect the relatively stable nature of PbSO₄ the primary weathering product of galena.
- The treatment of the tailings with low rates of lime (½ pH-6) was found to significantly increase the availability of Fe and sulphate concentrations in the tailings. This result, combined with the generally higher quantities of acidity generated in this same treatment, indicates that sulphide oxidation may have been enhanced by lime application. This finding has profound implications for any future attempts to reclaim the Tui mine site as it indicates that the use of liming agents either to establish vegetation or to try and mitigate AMD could exacerbate already phytotoxic growing conditions and/or AMD unless sufficiently high liming rates are used.

CHAPTER 7

Plant Growth Trials

7.0 Introduction

As discussed in Chapter 3 (section 3.7), metalliferous wastes resulting from mining activities that contain elevated concentrations of one or more heavy metals are notoriously difficult to reclaim (Williamson & Johnson, 1981). The establishment of vegetation on pyrite-bearing tailings, such as the Tui tailings, is particularly difficult because the release of sulphuric acid during the oxidation of pyrite often leads to acidification of the growing medium (Maclean & Dekker, 1976). In addition to low pH and metal toxicity, plant growth in metalliferous wastes is commonly limited by other factors which include poor physical structure, low nutrient availability and limited water holding capacity (Whiteley & Williams, 1993). Characterisation of the Tui mine tailings indicates that the main factors limiting plant growth in the Tui Mine tailings are associated with the tailings' chemical characteristics as opposed to their physical characteristics (Chapter 4).

Chemically, the Tui Mine tailings are an extremely inhospitable plant growth medium, due primarily to their very low pH and elevated content of phytotoxic metals (Chapter 4; section 4.3). Problems associated with low pH are exacerbated in the tailings due to their low clay and almost negligible organic matter contents which results in the tailings being very weakly buffered against pH change and reduces the ability of the material to bind potentially toxic metal ions. Without chemical amendment, ongoing sulphide oxidation and the migration of acidic, metal-contaminated pore waters within the surface tailings is likely to prevent widespread vegetative colonisation of the tailings within the near future. Overseas observations indicate that should a plant cover become established without intervention, the cover is likely to be sparse and lacking species diversity (Sengupta, 1993).

To gain the full aesthetic and practical benefits of a vegetative cover, the cover should be continuous, dense and permanent. Ideally vegetative stabilisation should produce a self-perpetuating plant cover either directly, or by promoting the colonisation of plants

which will form a self-regenerating community (Darmer, 1973). A vegetative cover on the Tui Mine tailings, besides being useful for stabilising the material against wind and water erosion, assisting in the immobilisation of potentially toxic cations, reducing the subsequent risk of groundwater pollution and improving the aesthetic appearance of the site, may also serve to reduce the rate of biochemical sulphide oxidation (Ritcey, 1989). A review of literature discussing the potential benefits and disadvantages of establishing vegetative covers on mine wastes is included in Chapter 3 (section 3.7).

Chapter Overview

This chapter reports the aims, designs, methodologies and results of two glasshouse pot trials that were conducted to investigate the feasibility of revegetating the Tui mine tailings. The first trial (Trial One) is reported in section 7.6 and was designed to investigate the effects of lime addition to the Tui tailings in terms of this amendment's ability to ameliorate adverse growing conditions. Four rates of lime were studied including a nil rate and an extremely high rate (112 Mg/ha) that was based upon the acid generating potential of the tailings material. A second and pivotal aim of Trial One was to assess the germination and growth attributes of 5 plant taxa, including 2 varieties of metal-tolerant grass and a low fertility forage legume. A comparative assessment of the metal-tolerant taxa was made with two non-tolerant grass cultivars.

The primary aim of the second trial (Trial Two), reported in section 7.7, was to investigate the germination and growth response of two plant species (*Festuca rubra* var. Merlin and *Lotus corniculatus*) on tailings amended with varying rates of composted sewage sludge. The effects of four rates of sludge were assessed both with and without addition of lime. The highest sludge rate was designed to raise the organic matter content of the tailings to 4%, a level comparable to that found in many humic and mineral soils. In those treatments receiving lime, lime was added at a rate designed to elevate the pH of the media to 6. The aims and designs of Trials One and Two are outlined in greater detail in sections 7.6 and 7.7 respectively.

Ensuing sections 7.1 to 7.5 background the characteristics of the various trial materials and present methodologies and relevant information common to both trials. Treatment selection methods and monitoring procedures used to assess the effects of the various

amendments on the tailings' plant growth characteristics are also presented. Methodology specific to the individual trials are reported within sections 7.6 and 7.7.

7.1 Materials

The characteristics and origin of the tailings and amendment materials used in the two trials are outlined below.

7.1.1 Tailings Selection

Approximately 500 kg of Tui tailings were collected from the top 200 mm of the tailings profile at the dam site. This involved collecting 20 kg samples at localities adjacent to the 12 sampling sites set up on the surface of the tailings dam (Figure 4.1). After collection and transportation, the samples were combined and stored at 4 °C prior to the initiation of the trials. Two weeks before commencing the pot trials the tailings were sieved to less than 4 mm and mixed thoroughly to create an homogenous growing medium.

Intact cores of tailings were not used for the plant growth experiments because chemical analysis of the grid samples indicated that the tailings were highly variable (Chapter 4). The chemical non-uniformity of the tailings is likely to have resulted in widely differing plant growth yields between replicate treatments. The variation encountered was not unusual as extreme variations in the chemical composition of mine wastes is common and variation within the site is often as great as between sites (Bradshaw & Chadwick, 1980; Smith & Bradshaw, 1979).

7.1.1.1 Characterisation of the Tailings

Several soil chemical analyses were conducted on the tailings used for the glasshouse pot trials immediately prior to amendment addition. The parameters measured included pH, electrical conductivity, acid generating potential, total elemental concentrations as assessed by ICP-AES¹ analysis and 25% v/v nitric acid and 0.1M hydrochloric acid extractable Fe and Cu concentrations estimated using FAAS².

¹ Inductively-coupled argon plasma atomic emission spectrometry

² Flame Atomic Absorption Spectrometry

(i) ICP-AES Analyses

ICP-AES analyses indicated that the levels of most elements in the tailings used for the glasshouse trials were comparable to concentrations found in the surface sample (0-50 mm) from preliminary sampling site S2 (Tables 4.2 and 7.1). Some elements, however, were present in much greater concentrations [mg/kg] in the tailings obtained from preliminary sampling site S2. These elements included Al (21334), B (2130) and Na (1536). In contrast, Pb (2082), S (3927) and Zn (204) were present at much lower concentrations in the S2 surface sample than in the trial tailings.

Certain elements were found in very high concentrations in the trial tailings, reaching or exceeding critical levels identified in soils delineating the onset of phytotoxicity (Table 7.1). These elements included As, Cd, Cu, Mo, Pb and Zn. Total Pb concentrations in the trial tailings were exceptionally high (13385 mg/kg), exceeding median soil concentrations by almost 400 times. In contrast the concentrations of Al, Fe, Cr, Mn, Ni and Sn were much lower than those generally found in soils (Table 7.1).

Table 7.1 Elemental concentrations within the Trial Tailings as determined by ICP-AES. Bracketed data represent 25% Nitric acid extractable Cu and Fe concentrations determined by FAAS.

Element	Tailings (0-200 mm) [mg/kg]	Medium Soils* [mg/kg]	Normal Range* [mg/kg] or %	Critical Levels † [mg/kg]	Critical Soil Solution Levels [mg/L]
Al	4090	-	† 0.45-10 %	-	0.1 - 30
As	185	6.0	0.1- 40	15 - 50	0.02 - 7.1
B	4.1	10.0	0.9-1000*	25 - 100	1 - 5
Ca	71	-	0.1 - 5 %*	-	1000*
Cd	5.2	0.35	0.01 - 2.0	3 - 8	0.2 - 9
Co	2.7	8.0	0.5 - 65	25 - 50	0.1 - 3
Cr	3.3	70	5 - 1500	75 - 100	0.5 (VI)
Cu	249 (235)	30	2 - 250	60 - 125	0.5 - 8
Fe	13418 (13934)	40000	0.4 - 8.7 %*	-	20
K	875	-	0.1 - 4.0 %*	-	-
Mg	93	-	0.1 - 1.0 %*	-	64*
Mn	4.9	1000	2 - 10 000	1500 - 3000	1 - 100
Mo	13.8	1.2	0.1 - 40	2 - 10	0.5 - 2
Na	118	-	-	-	-
Ni	1.4	50	2 - 750	100	0.5 - 2
P	91	-	200-1500*	-	-
Pb	13385	35	2 - 300	100 - 400	3 - 20
S	9427	-	100-1000	-	-
Se	<10.0	-	0.1 - 5	5 - 10	1 - 2
Sn	2.7	-	1 - 200	50	-
Sr	18.8	-	2-600†	-	-
Zn	662	90	1 - 900	70 - 400	60 - 400

Sources: * = Bowen (1979); † = Kabata-Pendias & Pendias (1984); • = Robertson (1985);
♣ = Förstner (1995); ♦ = McLaren & Cameron (1996)

Although the metal concentrations listed in Table 7.1 are a useful guide for identifying anomalously high levels of specific metals that are potentially phytotoxic, the use of this data to predict plant availability is, at best, very limited (Chapter 3; section 3.4.2). It is well recognised that the toxicity of a specific element to plant growth is more dependent on its nature and availability in the soil solution than on its total concentration in the tailings medium (Brooks, 1987). In the case where a plant growth medium is contaminated with phytotoxic concentrations of several elements (as it clearly is in the Tui mine tailings), predicting plant uptake of these metals is further complicated by metal interactions that can occur both at the root surface and within the plant (Mengel & Kirkby, 1987; Luo & Rimmer, 1995).

Interactions between macronutrients, micronutrients and non-essential elements occur due to the non-specific uptake process of most ions that depends primarily on the concentrations of the ion species in the nutrient solution and in some cases on the specific permeability of plant membranes to specific ions (Mengel & Kirkby, 1987). These interactions can be further defined as being either ‘antagonistic’ or ‘synergistic’. Antagonistic interactions are more commonly observed and occur when high concentrations of one ionic species in the soil solution reduces the ability of a plant to take up another ionic species (Mengel & Kirkby, 1987). Despite the fact that much research has been conducted investigating the multitude of interactions that are known to occur (eg. Zn^{2+} and Cd^{2+} , NO_3^- and Cl^-), soil variability and the complexity of the interactions often makes it very difficult to predict plant uptake from soil test concentrations, regardless of the type of extractant used (Kabata-Pendias & Pendias, 1984; Mengel and Kirkby, 1987). Thus, the use of total elemental analysis to predict plant uptake of specific metals and metal toxicity is clearly inappropriate.

(ii) Acid Generating Potential

The ‘total’ Fe and Cu concentrations in the tailings as determined by extraction with 25% v/v nitric acid and FAAS analysis compared well with ICP-AES values (Table 7.1). The tailings were found to contain about 70 mg/kg and 1795 mg/kg of 0.1M HCl extractable Cu and Fe respectively. These values were used in conjunction with the 25% nitric acid extractable Cu and Fe concentrations to predict the theoretical acid generating potential (TAGP) of the trial tailings as per the method outlined in Chapter 4 (section 4.4.1).

The results indicate that between 28.7 and 43.2 Mg CaCO_3 /1000 Mg of tailings material is required to neutralise the acid produced from the complete oxidation of pyrite and chalcopyrite in the trial tailings. The lower value assumes that all of the Fe is precipitated as hydronium-jarosite, whereas the higher value assumes that ferric Fe completely hydrolyses to form ferrihydrite (section 4.4).

The higher of the two predicted TAGP rates (43.2 Mg CaCO_3 /1000 Mg of tailings) was used as one of four lime amendment rates in Trial One. Based on a lime incorporation depth of 200 mm and assuming that the tailings have a uniform bulk density of 1.3 Mg

per cubic metre, this rate is equivalent to applying approximately 112 Mg of lime per hectare.

(iii) pH Buffering Capacity

The pH buffering capacity of the unamended tailings was calculated as per the method outlined in Appendix 6(A) and was used to estimate the liming requirement of treatments within both trials. The unamended tailings were found to exhibit a pH buffering capacity of 6.33 tons of CaCO_3 /1000 tons of tailings. This value represents the amount of lime required to raise the pH of the tailings to 6.0. The fact that relatively low quantities of lime were found to induce a large change in pH indicates that the tailings are poorly buffered as a result of being dominated by quartz. If the tailings had have contained higher concentrations of organic colloids and/or clay minerals these materials would have served to buffer the concentrations of hydroxyl and hydrogen ions in solution and hence inhibited pH change (Chapter 3, section 3.7).

The pH buffering capacity of tailings amended with 3 rates of sewage sludge (110, 220, 440 Mg/ha) was also assessed to enable liming rates for an additional three treatments in Trial 2 to be calculated (section 7.7). The incubation experiment demonstrated that in the short term (48 hours) the pH buffering capacity of the Tui mine tailings was not significantly altered by the addition of composted sewage sludge, as indicated by the near parallel nature of the best fit curves for each treatment (Figure 7.1a). The sludge was, however, found to act as a liming agent, raising the pH of the sludge/tailings mixtures. The liming effect of the sludge is evident in Figure 7.1a which shows that at the highest sludge application rate (440 Mg/Ha) the pH of the tailings can be raised to a pH of 6.0 using less than a third of the lime required to raise the pH of the untreated tailings to a comparable level. The liming rate reported in Figure 7.1a is based on the amount of lime required to raise the pH of 1000 Mg of sludge-amended tailings to approximately 6.0.

7.1.2 Lime (Calcium Carbonate)

Varying rates of finely ground ($<150\ \mu\text{m}$) analytical grade calcium carbonate were incorporated into the tailings used in this glasshouse pot trial. The purity and fine texture

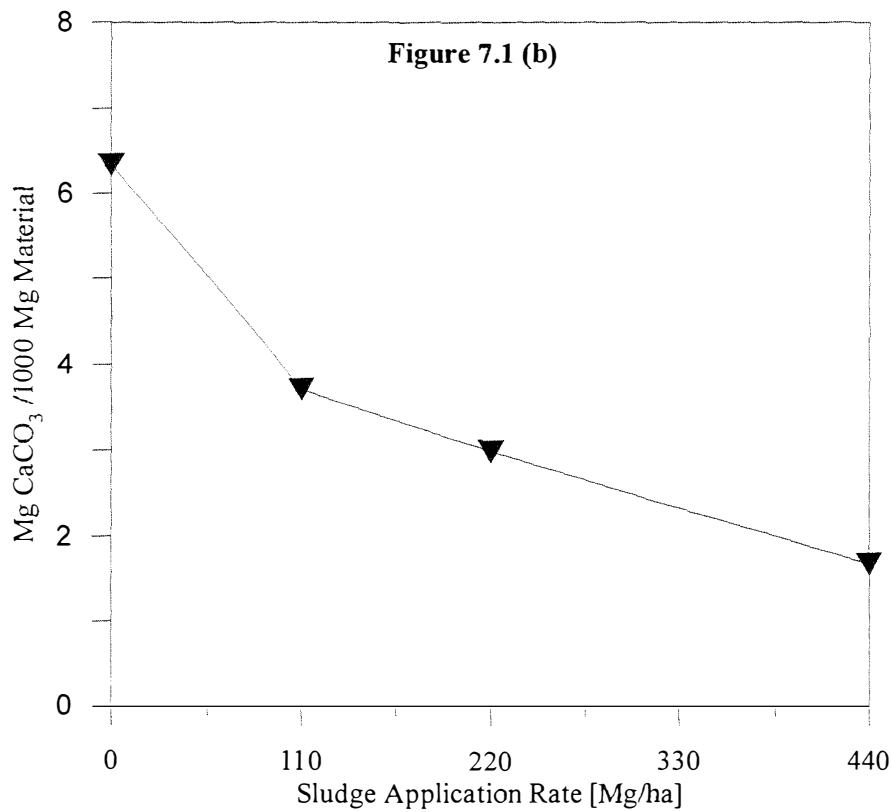
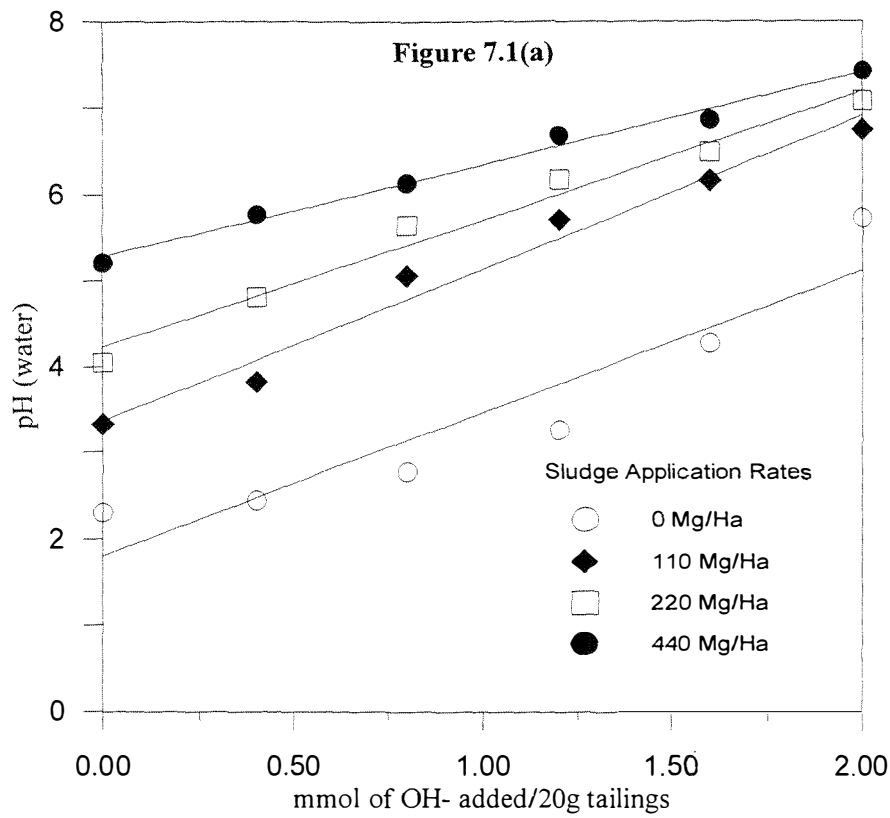


Figure 7.1 (a) The pH buffering capacity of the tailings amended with four rates of composted sewage sludge. The parallel nature of the best fit curves indicates that the pH buffering capacity of the tailings was not markedly improved by the addition of sludge in the short-term. **(b)** Relationship between the rate of sludge application and the amount of lime required to attain a pH of 6.

of the lime enabled the calculated liming requirements to be accurately met and ensured rapid dissolution of the liming material.

7.1.3 Composted Sewage Sludge

The composted sewage sludge used in Trial Two was sourced from Auckland’s North Shore City Council (NSCC) waste-water treatment plant. The majority of the waste-water treated by the plant is domestic in origin and thus the 200 m³ of sludge generated by the plant each day is considered to contain relatively low concentrations of heavy metals (Table 7.2). Treatment of the sludge includes stockpiling of the material for two years prior to use or disposal. Although the sludge was originally available to the public for domestic gardening and landscaping concerns about the safety and possible mismanagement of the material prompted the NSCC to discontinue making it available (Limpus-O’Reilly, 1997).

Table 7.2 Summary of the properties of the North Shore Sewage Sludge (Limpus-O’Reilly, 1997)

Properties	North Shore Sludge
pH (KCl)	6.4
Total Phosphorus [%]	1.23
Olsen Phosphorus [mg/kg]	274
Phosphorus retention [%]	43
Mineral Nitrogen [mg/kg]	216
Total Nitrogen [%]	1.87
Organic Carbon. [%]	23.6
Organic Matter [%]	40.7
EC [μS/cm]	173
Total Metals [mg/kg] As, Cd, Cr, Cu, Ni, Pb, Zn	29, 4.7, 153, 606, 135, 239, 1517
0.1 M HCl Extractable As, Cd, Cr, Cu, Ni, Pb, Zn	20, 2.6, 3, 12, 77, 41, 607

The beneficial effects and problems associated with the addition of sewage sludge to soils and mining wastes are discussed in Chapter 3 (section 3.7.4).

7.2 Trial Methodologies

This section outlines general methodologies and information relating to the housing and maintenance of the two glasshouse trials.

7.2.1 Water & Fertiliser Regime

The ‘field capacity’ (0.05 bar water content) of the various sludge and lime amended treatments was assessed using Haine’s apparatus to enable optimum moisture contents for the treatments to maintained during the growth experiment. Initially, the moisture contents of all pots were adjusted to 80% of the 0.05 bar water contents (Table 7.3). Due to the fine-grained nature of the non-sludge amended treatments, however, this water content was found to excessively wet the plant growth medium. Reduction of the moisture content of these treatments to approximately 70 % ‘field capacity’ improved the physical consistency and ‘handling’ properties of the tailings.

Table 7.3 Percentage water content (oven dry basis) of the amended tailings at 0.05 bar pressure. 80% values and the approximate water content used in the trials are also provided.

Sludge Rate [Mg/ha]	Water content at 0.05 bar	80% 0.05 bar content	Approx. Water Content Used
Nil	19.3 %	15.5 %	13 %
110	22.6 %	18.1 %	16 %
220	25.0 %	20.0 %	18 %
440	28.5 %	22.8 %	20 %

To try and ensure plant nutrients were non-limiting, all treatments received a complete nutrient solution based on that developed by Middleton (1973). Approximately 50 ml of the solution was applied daily to the pots and any moisture deficits were remedied by the addition of distilled water to bring the treatment pots up to optimum moisture content. Thus during the course of the trial each pot received in the vicinity of 2.5 litres of growth solution containing about 1.0 g NH_4NO_3 , 0.3 g of KH_2PO_4 and K_2HPO_4 and 0.2 g of K_2SO_4 to cater for the plants’ N, P and K nutritional requirements. Other macronutrients including a relatively high rate of magnesium and several micronutrients were also applied to the tailings at recommended concentrations (Middleton, 1973). Where practicable the trial pots were treated identically in terms of watering and

nutrient application. During the later stages of the trials, however, some of the heavily foliated pots required substantial quantities of additional water to compensate for water lost via transpiration.

To prevent the build-up of excessive levels of soluble salts on the surface of the trial pots, the various treatments were flushed with distilled water (approximately 3 x pore volume) twice during the course of the trial. The first of these flushes was conducted 4 weeks after sowing when electrical conductivity values in the control pots were found to exceed 2000 $\mu\text{S}/\text{cm}$ (Figure 7.2). The pots were flushed again 2 weeks before end of the growing term. Monitoring of the electrical conductivity of the various treatments is discussed further in section 7.5.2.

7.2.2 Glasshouse Environment

The pot trials were conducted in a glasshouse maintained at 25°C during the late summer and early autumn of 1995. Diurnal temperature variation in the glasshouse were as much as 10-15 °C. The pots were maintained in a completely randomised order and rotated often to minimise growth differences resulting from positional effects within the glasshouse.

7.3 Plant Species Selection

As discussed in Chapter 3 (section 3.7.5) the use of metal-tolerant grass populations for the revegetation of metalliferous mine waste is well established in the United Kingdom (Gemmell, 1977; Johnson *et al.*, 1977; Smith & Bradshaw, 1979). Relatively little work, however, has been conducted to investigate the viability of using such taxa for mine revegetation work here in New Zealand. Three varieties of metal-tolerant grass (*Agrostis capillaris*³ var. Parys Mountain, *A. capillaris* var. Goginan and *Festuca rubra* var. Merlin) were imported into the Country to investigate the potential use of these plant taxa for revegetating the Tui Mine tailings.

An initial assessment of seed viability and the metal tolerance of the plant species was conducted by monitoring seed germination on filter papers saturated with varying concentrations of Cu, Pb and Zn nitrate. A qualitative assessment of the species'

tolerance to these metals was based on percentage germination and seedling vigour. Because the trial was non-replicated the results were only used as a guide for species selection. The two non-metal-tolerant grass species (*Agrostis capillaris* var. Egmont and *Festuca rubra* var. Lobi) that were used in the glasshouse trials were also evaluated in the germination experiment which is outlined below.

7.3.1 Seed Germination Trial

Stock solutions of 1000 mg/L Cu, Pb and Zn nitrate solutions were prepared using analytical grade $\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ reagents and distilled water. The stock solutions were diluted with distilled water to yield solutions containing 0, 5, 10, 20, 50 and 100 mg/L Cu, Pb and Zn. Two filter papers were placed in each of ninety petri dishes and 5 ml of the treatment solutions were added to the dishes to fully moisten the filter papers. Approximately 100 seeds of each of the five plant taxa were then distributed evenly on the treated filter papers to yield 15 series of six petri dishes varying in concentration from 0 to 100 mg/L (Appendix 7(A)). It was postulated that metal concentrations greater than 100 mg/L were not likely to occur in the 'soil solution' of the Tui tailings. The individual dishes were then covered and stored at ambient room temperature (20 °C) on a laboratory bench, out of direct sunlight. Water losses due to evaporation were minimal, however, the periodic addition of distilled water was required.

At the termination of the trial (4 weeks after sowing) seed germination on each of the dishes was classified into one of four categories, *high*, *medium*, *low* and *nil*. Dishes exhibiting > 75 % germination with seedlings exhibiting fully-expanded, green cotyledons were classed as having *high* germination. The *medium*, *low* and *nil* classes represent 25 - 75% germination, < 25% germination and nil germination respectively.

7.3.2 Trial Results

(i) Germination

No obvious differences in germination time were noted amongst the five plant taxa. The majority of seeds germinated within ten days of sowing. With the exception of

³ Synonymous with *Agrostis tenuis*.

A. capillaris var. Goginan there was a high germination rate for all other taxa on the nil treatments (distilled water). This indicated that a significant proportion of the Goginan seed was non-viable. The low viability of the seed was confirmed by germination tests run subsequent to the trial. These tests indicated that only about 30% of the Goginan seed was viable compared with 93% and 90% for *A. capillaris* Parys Mountain and Egmont respectively and 85% and 78 % for the two varieties of *F. rubra* (Merlin and Lobi).

(ii) Lead & Zinc Tolerance

With the exception of *A. capillaris* (Goginan), all five plant taxa were found exhibit *high* germination rates in solutions of up to 100 mg/L Pb and Zn nitrate. Despite expected tolerance to relatively high concentrations of Pb, Goginan exhibited only *medium* germination and vigour in the 0, 5, 10, 20 and 50 mg/L Pb treatments. A visual assessment of the 100 mg/L Pb treatment indicated that less than 10% of the Goginan seed germinated.

(iii) Copper Tolerance

Of the three heavy metals investigated, Cu was found to have the most detrimental effect on the seed germination, with three out of the five plant taxa exhibiting *nil* or *low* germination at Cu concentrations above 10 mg/L (Appendix 7(A)). The only variety to germinate above 20 mg/L Cu was Merlin, the metal-tolerant cultivar of *F. rubra*. This taxa demonstrated *high* germination at 50 mg/L, however, no germination was evident at 100 mg/L.

Of the two metal-tolerant varieties of *A. capillaris*, var. Parys Mountain again fared better than Goginan. Results suggest that the germination threshold for Goginan lies between 10 and 20 mg/L Cu as indicated by *low* germination at 10 mg/L and no germination at 20 mg/L. Parys Mountain exhibited *medium* germination at 20 mg/L Cu, however, no germination was evident on the 50 mg/L treatment. The non metal-tolerant varieties of *F. rubra* and *A. capillaris* showed little tolerance to Cu concentrations above 10 mg/L, with Lobi failing to germinate and Egmont demonstrating *low* germination only at 20 mg/L (Appendix 7(A)).

7.3.3 Discussion of Germination Results

It is apparent that a greater range of solution concentrations were required to fully investigate the tolerance of the plant taxa to Pb and Zn. *High* rates of germination were noted for all seeds on the Pb and Zn treatments with the notable exception of *A. capillaris* var. Goginan. In the case of Cu, the 0-100 mg/L range used in the experiment proved adequate to assess the tolerance of the seed to this metal, as Cu was found to inhibit seed germination at much lower concentrations than Pb and Zn. It is widely accepted that Cu tends to be more phytotoxic than Pb and Zn due to its tendency to displace other metal ions and particularly Fe from physiologically important centres (Neuman *et al.* 1987; Mengel & Kirkby, 1987).

Based on experimental results the taxa seed have been placed in the following predicted order of increasing tolerance to heavy metals:

Most Tolerant* ← *Least Tolerant

Merlin < Parys Mountain < Egmont < Lobi < Goginan

F. rubra var. Merlin and *A. capillaris* var. Parys Mountain were found to exhibit greater tolerance to heavy metals than their equivalent pastoral varieties (Egmont and Lobi). The poor performance of *A. capillaris* var. Goginan is believed to reflect the low viability of the seed. Plants germinated from low viability seeds often exhibit poor vigour and thus tend to fair relatively poorly in adverse growing conditions.

Based on the results of this trial it was decided to exclude *Agrostis capillaris* var. Goginan from the plant growth trials due to its low seed viability and poor performance. *A. capillaris* var. Parys Mountain was obviously likely to show greater tolerance to the extreme growing conditions provided by the tailings. The characteristics of the various taxa used in the trials are outlined below (Table 7.4).

Table 7.4 Description of Plant Taxa used in Glasshouse Trials.

Plant Taxa	Characteristics
<i>Agrostis capillaris</i> var. Egmont (bent grass, browntop)	<i>A. capillaris</i> is a low fertility perennial grass often found growing on acidic to neutral substrates in temperate regions. It is generally shade tolerant and moderately resistant to drought (Bennett <i>et al.</i> , 1978). Most varieties do well under heavy traffic, however the Egmont variety is best suited to amenity areas that do not get severe wear (DSIR Grasslands, 1989).
<i>Agrostis capillaris</i> var. Parys Mountain (bent grass, browntop)	<i>A. capillaris</i> var. Parys Mountain (PM) is classified as a pseudometallophyte because populations can be found on both metalliferous and ‘normal’ sites (Antonovics <i>et al.</i> , 1971). The PM variety was isolated from the Parys Copper Mine located in the Anglesea region of northern Wales. It is commercially available and has been used extensively in Great Britain to cover metalliferous wastes (Smith & Bradshaw, 1979; Whiteley & Williams, 1993). PM is recognised mainly for its Cu tolerance, although it does exhibit some tolerance to other metals including Pb and Zn. Metal-tolerant bent grass has been shown to successfully root in solutions containing up to 0.5 mg/L Cu and in tailings containing 1 % Pb and 1% Zn (Bradshaw & Chadwick, 1980).
<i>Festuca rubra</i> var. Lobi (Chewing or red fescue)	<i>F. rubra</i> is a low fertility grass that is generally found on neutral or slightly calcareous substrates. It is resistant to both drought and shade, developing a deep fibrous root system ideal for holding soils in place (Bennett <i>et al.</i> , 1978).
<i>Festuca rubra</i> var. Merlin (Chewing or red fescue)	Although this taxa has been isolated growing in substrates of low pH (4.5), <i>F. rubra</i> var. Merlin generally prefers alkaline growing conditions. This cultivar was isolated on abandoned mine-sites in the UK and was specifically bred for revegetating Pb and Zn contaminated alkaline substrates (Bradshaw & Chadwick 1980; Gemmell, 1977; Bradshaw & McNeilly, 1981).
<i>Lotus corniculatus</i> var. (Birdsfoot trefoil)	<i>L. corniculatus</i> is an acid tolerant, low fertility perennial forage legume used for pasture, hay and silage in the US and in grass-legume mixtures on disturbed land areas, particularly acid strip mine soils. It is adaptable, growing on poorly drained, droughty and both acid and alkaline soils. Isolated plants have reportedly been found growing on acid strip soils with pH 3.5 (Bennett <i>et al.</i> , 1978). <i>L. corniculatus</i> is useful for vegetative stabilisation as it often exhibits well developed taproot systems with numerous lateral branches. Rooting depths can exceed 1 m.

The rationale for the use of metal-tolerant plants and the mechanisms and limitations of metal tolerance are reviewed in Chapter 3 (section 3.7.5).

7.4 Sowing Rates & Dates

In both pot trials the equivalent to 100 viable seeds were sown into each of the pots. The variation in seed viability⁴ meant that the number of seeds sown had to be varied for each species. The total number of seeds required for each species were counted and weighed in triplicate to attain an average weight for each taxa (Table 7.5) . The seeds for each treatment were then weighed-out and placed in 4 ml vials until the time of sowing. The seeds of the two *Agrostis capillaris* varieties were mixed with a small quantity of quartz sand (2 grams) prior to sowing to improve seed distribution. In addition to

⁴Seed viability tests were conducted independently by the Seed Technology Centre at Massey University.

regular watering, the surface of the pots were sprayed with distilled water at least once a day during the germination period to ensure the seeds were kept moist.

Table 7.5 Seed viability and sowing rates for each of the plant taxa.
Seeds per pot = 100/ proportion viable seed

Plant Taxa	Approximate Number of seeds/gram	Seed viability [%]	Seeds required per pot	Mass of seeds [g]	Sowing rate [kg/ha]
<i>A. capillaris</i> (Parys Mountain)	12000	93	108	0.009	7
<i>A. capillaris</i> (Egmont)	14000	90	111	0.008	6
<i>F. rubra</i> (Merlin)	1100	85	118	0.111	84
<i>F. rubra</i> (Lobi)	1100	78	128	0.118	89
<i>L. corniculatus</i>	833	53	189	0.227	171

After the 3 week incubation period which commenced on the 26-01-95 the various treatments were transferred to the trial pots and the seeds were sown on the 16-02-95. The trials were terminated 8 weeks later, on the 13-04-95 when the final herbage cut was made. The unsown control pots were maintained for a further 13 weeks after harvesting and finally sampled on the 13-7-95.

7.5 Monitoring of the Growth Medium

During the course of the trial a number of tailings properties were measured to assess chemical changes in the growth medium with time. The properties measured included, pH, electrical conductivity (EC), exchangeable Ca, K, Mg and Na, cation exchange capacity (CEC), Olsen P, calcium phosphate extractable $\text{SO}_4^{=}$ concentrations, 0.1M HCl and 0.02M CaCl_2 extractable metal (As, Cd, Cu, Fe, Pb, Mn, Zn) concentrations and 1M KCl and 0.02M CaCl_2 extractable Al levels (Table 7.6).

Monitoring of the trial concentrated primarily on assessing the tailings chemical conditions in treated but non-sown pots (control pots). Four such pots were required for Trial One and 8 for Trial Two. The control pots were stored and treated similarly to sown pots but because the control pots were destructively sampled, water addition to

these pots had to be adjusted after each sampling to ensure that they were maintained at the desired water content (section 7.2.1).

Table 7.6 Sowing, termination and sampling dates for Glasshouse Trials. * The fertility measurements include Olsen P, CEC, exchangeable Ca, K, Mg and Na. † Metals include 0.1M HCl and 0.02M CaCl₂ extractable As, Cd, Cu, Fe, Pb, Mn and Zn levels and 1M KCl and 0.02M CaCl₂ extractable Al concentrations.

Parameters	Week 0 26-1-95	Week 3 16-2-95 (Sowing)	Week 4 23-2-95	Week 5 2-3-95	Week 7 16-3-95	Week 9 30-3-95	Week 11 13-4-95 (Final Cut)	Week 24 13-7-95
Fertility*		✓					✓	
Metals†		✓			✓		✓	
SO ₄ ²⁻		✓			✓		✓	
EC		✓			✓		✓	
pH	✓	✓	✓	✓	✓	✓	✓	✓

7.5.1 pH

The pH of the amended control pots were measured 7 times during the course of the two trials using a 1:2.5 tailings to water ratio as per the method outlined in Chapter 4 (section 4.1). To reduce processing time of the samples, prior to sampling, the water content of the various treatments were adjusted to 70 or 80 % field capacity and left to equilibrate for 30 mins. Weight adjusted samples (the equivalent of 10.0 g of air-dried material) of each treatment were then measured out into propylene beakers to ensure a constant tailings to water ratio amongst the treatments. Samples of standardised soil (Chapter 4.1.1) were included with each batch to ensure that comparisons could be made between the batches at different sampling periods.

In addition to measuring pH levels in the control pots, at the termination of the growing period pH measurements were also made from material taken from each of the 160 sown pots constituting the two trials. This enabled a comparative assessment between the control and the sown pots to be made (Table 7.7). Comparison of the pH values in Table 7.7 indicate that at the end of the growing period the pH values in the control pots were very close to values observed in the sown pots. This findings is significant in that it indicates growing conditions in the control pots were similar to those in the sown pots and justifies the use of extrapolated data from the control pots to examine the effect of tailings characteristics on plant growth.

To assess the long term pH stability of the various treatments, an additional set of pH measurements were made in the control pots approximately 3 months after the termination of the trials. During this time maintenance of the control pots at 25°C and at 70 - 80 % field capacity moisture was continued. Graphs tracing the variation of pH with time for the various lime and sludge amendments are included and discussed separately in the two respective trials.

7.5.2 Electrical Conductivity

The electrical conductivity (EC) of the lime and sludge amended control pots were assessed at week 3 (sowing), week 7 and week 11 (termination) of the trial. To corroborate EC results obtained from the unsown control pots, 18 sown pots from both trials were destructively sampled after harvesting (Table 7.7). Two samples , a surface (0-10mm) and subsurface sample (>50 mm) were collected from each of the pots to investigate depth-wise EC variation within the amended tailings.

The conductivity of the samples was assessed using a 1:5 ratio of sample to water. The method involved weighing 5 g air-dry ground (<2mm) samples of the amended tailings into 50 ml centrifuge tube. Twenty-five ml of deionised water was then added and the samples were shaken for 30 minutes prior to gravity filtration through Whatman #1 filter paper. The conductivity and temperature of the filtrates were measured with a Hanna Instruments HI-8633 portable conductivity meter. Because the meter had an in-built temperature compensation mechanism, standardisation of the individual EC values to 25°C was unnecessary. Prior to each use, however, it was necessary to calibrate the meter using a solution of standardised 0.01M KCl. The electrical conductivity of each sample was then calculated as per equation 7.1

$$EC = EC_s \times j \tag{7.1}$$

- EC = sample electrical conductivity
- EC_s = solution electrical conductivity
- j = meter calibration coefficient

Based on a ranking system outlined in Blakemore *et al.*, (1987), the amended materials were found to exhibit EC's that were either high (>800 μS/cm) or very high (>2000

μS/cm) throughout the duration of the trial (Table 7.7). Comparison of the sludge’s EC (173 μS/cm) to that of the unamended Tui tailings (1257 μS/cm) indicates that the high electrical conductivity of the treatment solutions is largely attributable to the inherently high soluble salt content of the tailings.

Table 7.7 The pH and electrical conductivity (EC) of the tailings treated with different amendments in the presence of plants (sown pots) and in the absence of plants (control pots). The average pH values of the 160 sown pots are also presented along with standard deviation values. Average pH calculations: n = 24 and n = 8 for glasshouse Trials 1 and 2 respectively.

Trial	Sludge [Mg/ha]	Lime [Mg/ha]	Electrical Conductivity [μS/cm]			pH (8 weeks)	
			Sown Pots (surface)	Sown Pots (subsurface)	Controls Pots	Sown Pots	Controls Pots
1	NA	0	3522	2272	1748	2.19 ± 0.02	2.13
1	NA	8.25	3487	2319	1993	2.27 ± 0.03	2.16
1	NA	16.5	1069	1290	1112	6.60 ± 0.13	6.59
1	NA	112	1749	1806	1468	7.59 ± 0.05	7.49
2	0	0	3363	2266	1948	2.22 ± 0.02	2.08
2	110	0	3894	2266	2513	2.22 ± 0.03	2.13
2	220	0	794	1074	1054	3.78 ± 0.35	3.80
2	440	0	1156	1297	1215	4.71 ± 0.05	4.56
2	0	16.5	1292	1181	1267	6.56 ± 0.10	6.46
2	110	10.1	989	1208	1048	4.36 ± 0.16	4.30
2	220	8.5	1382	1185	1270	4.73 ± 0.14	4.37
2	440	5.1	1566	1292	1384	4.98 ± 0.06	4.87

Comparison of the surface and subsurface EC values in Table 7.7 indicates that those pots receiving low rates of lime and sludge generally exhibited higher EC at the surface of the pots. The higher EC’s encountered suggest that soluble salts were migrating upwards in the substrates due presumably to convective flow (capillary rise) resulting from the evaporative loss of water at the surface of the pots. Such effects are commonly noted in disturbed mining materials and are a frequently encountered problem in glasshouse experiments in which downward salt movement associated with convection (leaching) is minimal (Carlstrom *et al.*, 1987). The minimal build-up of salts at the surface of the heavily limed or sludge treated tailings is believed to reflect the lower concentrations of electrolytes in solution.

The changes in EC values for various treatments during the growth periods are presented in Figure 7.2. In general there was an initial increase in EC values followed by a decrease towards the termination of the trial. The trends in EC values were similar to those of phosphate extractable sulphate contents of various treatments (Figure 7.3). This clearly indicates that a considerable proportion of the salts responsible for conducting electricity in the tailings were sulphates. Flushing the pots midway during the experiment (as discussed in section 7.2.1) clearly lowered the concentrations of sulphate in the tailings and simultaneously reduced EC in most treatments markedly.

Comparison of the EC values of the control pots with the sown pots once again indicates that growing conditions in the control pots were similar to those in the sown pots and further justifies the extrapolation of metal concentration data from the control pots.

7.5.3 Metal Concentrations

25% HNO₃ and 0.1 M HCl acid extractable metal concentrations were determined by the methods outlined in Appendices 4(E) and 4(F).

The metal extraction procedure using 0.02 M CaCl₂ was based on the method of Hoyt & Nyborg (1972) and involved the addition of 20 ml of the extractant to 10.0 g of tailings in a 50 ml polypropylene centrifuge tube. The solutions were shaken end-over-end for 1 hour at 25°C before being centrifuged at 9000 rpm for 5 minutes and filtered through Whatman # 42 filter paper.

1 M KCl extractable Al concentrations were assessed using a method based on that of McLean (1965) and outlined in Blakemore *et al.* (1987). The extraction procedure involved weighing 5.0 g of air-dried tailings into a 125-ml conical flask to which 25 ml of 1 M KCl was added. The contents of the flasks were gently mixed and then allowed to stand for 16 hours before being filtered through Whatman # 42 filter paper.

Aliquots of the supernatants were diluted as required and concentrations determined using flame atomic absorption spectrometry. An Al hollow-tube cathode lamp set at 10.0 mA was used in conjunction with a reducing nitrous oxide-acetylene flame to

determine 1M KCl and 0.02M CaCl₂ Al concentrations. Typical flame type and lamp current settings for other metals are provided in Table 4.9.

7.5.4 Seed Germination

The numbers of germinated seedlings were counted in each pot on 3 occasions during the first month of the experiment (1, 2 and 4 weeks after sowing). The results of germination are individually reported in each trial.

Throughout the duration of the trials, established seedlings were visually monitored for signs of interveinal chlorosis, discolouration and necrotic foliar tissue symptomatic of metal toxicities and/or nutrient deficiencies (Johnson *et al.*, 1977).

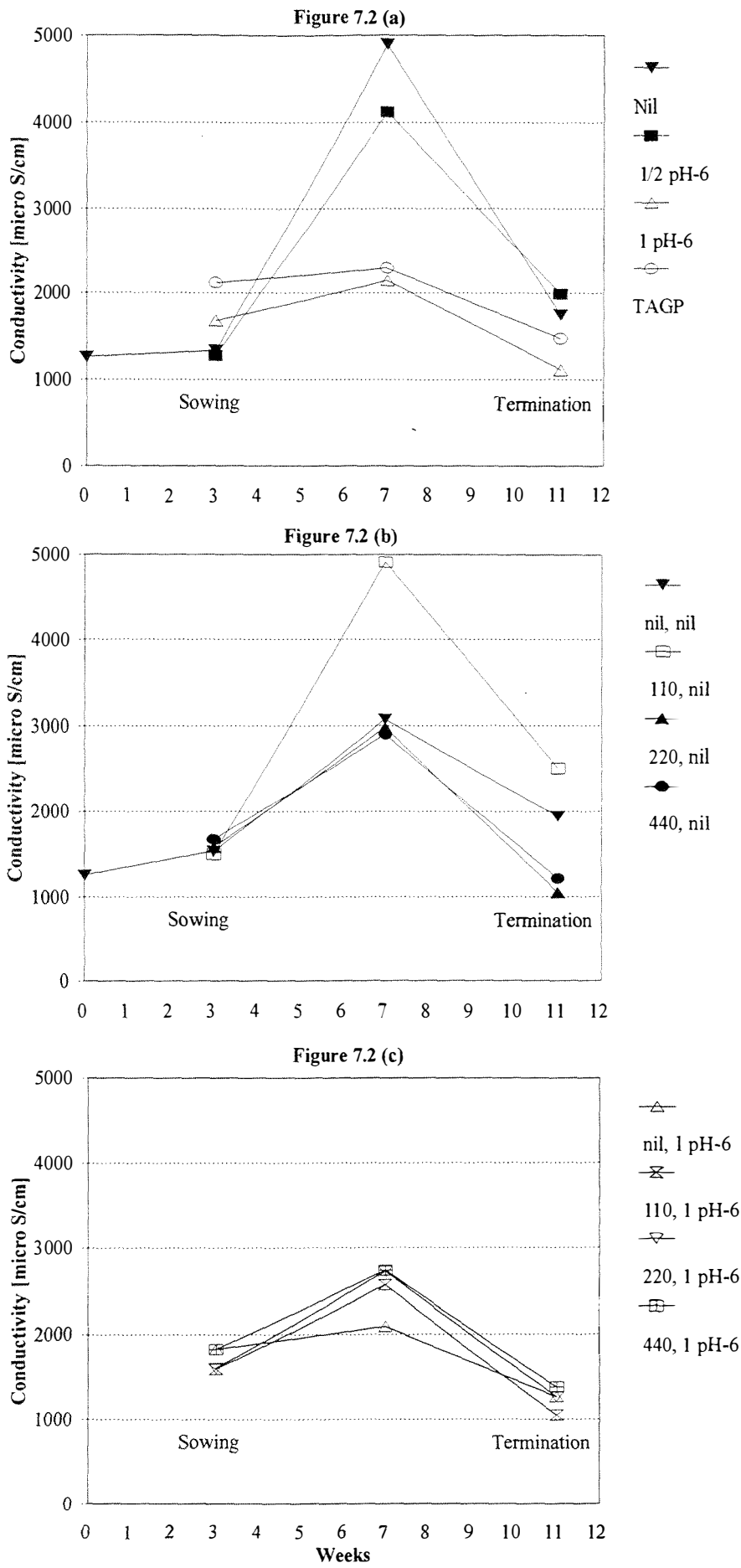


Figure 7.2 The changes in electrical conductivity of various glasshouse trial treatments. (a) Trial One: limed treatments, (b) Trial Two: non-limed/sludge amended treatments and (c) Trial Two: limed (1 pH-6 rate)/sludge amended treatments.

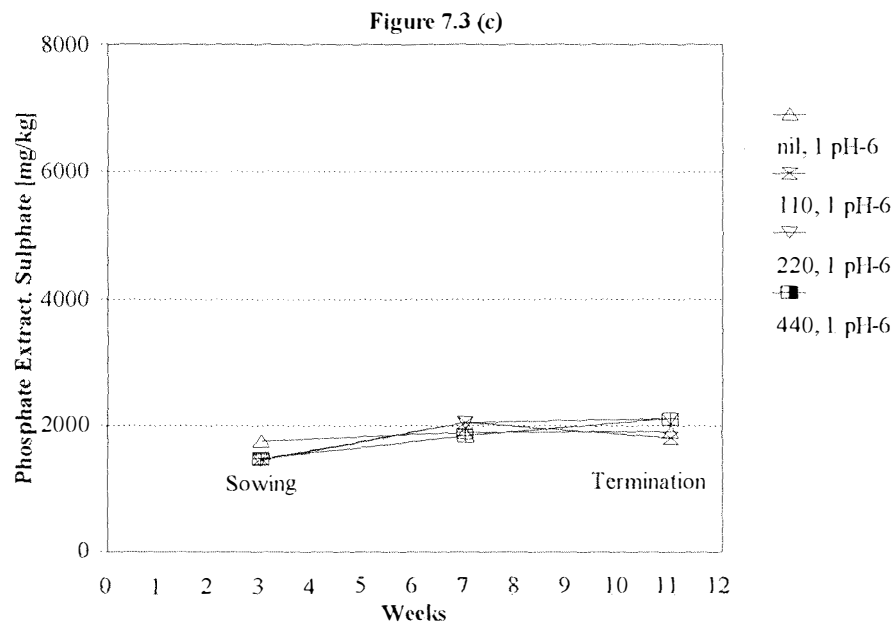
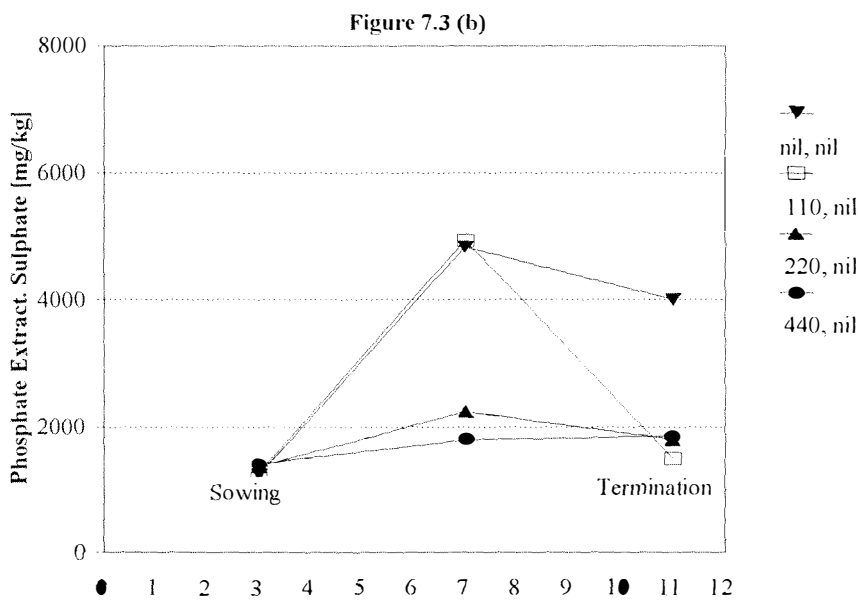
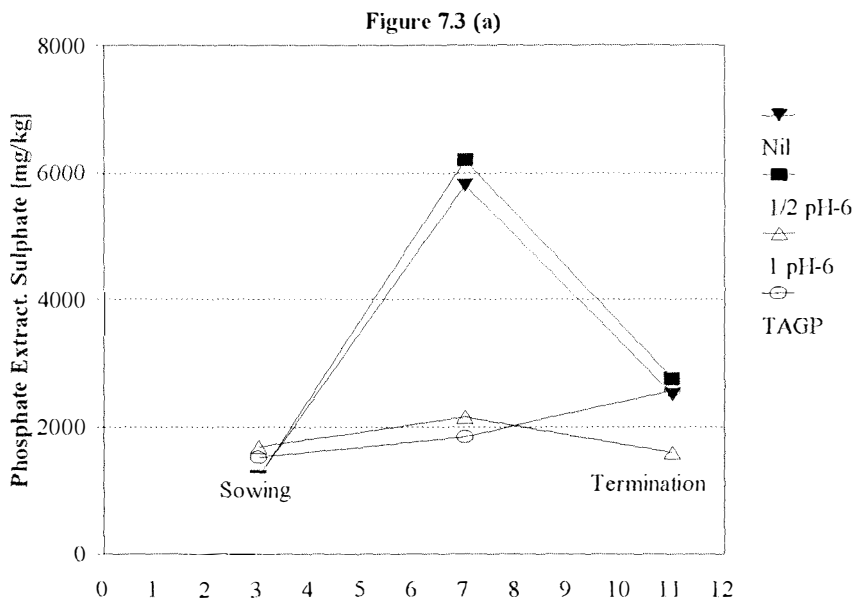


Figure 7.3 The changes in sulphate levels within various glasshouse trial treatments. (a) Trial One: limed treatments, (b) Trial Two: non-limed/sludge amended treatments and (c) Trial Two: limed (1 pH-6 rate)/sludge amended treatments.

7.6 Trial One - The Effects of Lime Application Rate and Plant Metal tolerance

7.6.1 Aim

This plant trial was specifically designed to investigate the impact of lime (CaCO_3) addition on the plant growth characteristics of the Tui mine tailings. Lime is an extremely useful soil amendment as it not only neutralises acidity but can also increase nutrient availability and hence plant uptake, reduce metal bioavailability and inhibit biooxidation of sulphide minerals (Chapter 3; section 3.7.3). Four rates of lime were assessed in this trial in conjunction with 5 varieties of plants, including two exotic metal-tolerant grass cultivars. This trial provided an excellent opportunity to assess the merits of using metal-tolerant grass varieties in place of conventional cultivars. Additionally it was anticipated that the results would aid in identifying an optimal liming rate that would facilitate germination and sustained plant growth.

7.6.2 Trial Design

To investigate the interaction of various liming rates, plant growth and metal tolerance, a completely randomised, factorially designed pot trial was conducted. Four liming rates and 5 plant taxa were assessed in the trial (Table 7.8). The characteristics of the plant taxa used in this trial, which included one legume (*Lotus corniculatus*), two metal-tolerant grass species (*Agrostis capillaris* var. Parys Mountain & *Festuca rubra* var. Merlin) and two non-metal-tolerant grass species (*Agrostis capillaris* var. Egmont & *Festuca rubra* var. Lobi), are discussed in Table 7.4. An additional treatment was included for *L.corniculatus* that consisted of inoculating the treated glasshouse trial tailings with rhizobium.

A total of one hundred pots were used in this trial (Plate 7.1). This included four replicates of each treatment and an additional four amended but non-sown *control* pots that were prepared for destructive analysis during the course of the trial.

Table 7.8 Design Treatments for Trial One

Liming Rate	Nil	½ pH-6 Rate	1 pH-6 Rate	TAGP Rate
Mg/ha	0	8.25	16.5	112
g/kg tailings	0	3.17	6.33	43.2
Plant Taxa	1, 2, 3, 4, 5	1, 2, 3, 4, 5	1, 2, 3, 4, 5	1, 2, 3, 4, 5
Lotus <i>Rhizobium</i> Treatment	+, -	+, -	+, -	+, -
Number of treatments	6	6	6	6

7.6.3 Methodology

7.6.3.1 Determination of Liming Rates

The glasshouse trial tailings were amended with four rates of analytical grade CaCO_3 (Table 7.8). The low and intermediate liming rates were based upon the pH buffering capacity of the tailings, with the intermediate rate of 16.5 Mg CaCO_3 /ha (1 pH-6 rate) representing the amount of lime required to raise the pH of the tailings to 6.0. The low rate (8.25 Mg CaCO_3 /ha) is equivalent to 50 % of the 1 pH-6 rate. The TAGP rate was the highest of the liming rates used and is based on the amount of lime required to neutralise the acid potentially produced from the oxidation of remnant sulphide minerals within the tailings. In theory the TAGP rate (112 Mg CaCO_3 /ha) is sufficiently high to prevent re-acidification of the tailings resulting from the total oxidation of acid generating sulphide minerals within the tailings.. The stated liming rates are based on lime incorporation to 200 mm depth and assume that the tailings have a uniform bulk density of 1.3 Mg/m³.

7.6.3.2 Lime Incorporation & Pot Preparation

The equivalent of 1 kg of oven dry tailings was weighed and placed into a series of numbered plastic bags. The various rates of lime (Table 7.8) were then added to the air-dried tailings and thoroughly mixed. After adjusting the water content of the various treatments to about 70% field capacity (section 7.2.1) with distilled water, the 100 bags were incubated at 25°C for 3 weeks.



Plate 7.1 Trial One 4 weeks after sowing. Comparative growth of the various taxa on uncontaminated soil is seen in the 4 plastic trays in the upper left hand corner of the photograph.

Upon completion of the 3 week incubation period the water content of the treatments was re-adjusted to 70% field capacity. The various treatments were then transferred to a series of numbered plastic pots of approximately 1300 cm³ which were lined with filter paper to prevent the loss of the amended growing media through the drainage holes. The combined weights of the plastic pots and treatments were then recorded to enable the watering requirements of the pots to be accurately met.

7.6.3.3 Sowing

Approximately 100 viable seeds of each taxa were sown on the surface of the appropriate treatment pots as per the methods outlined in Section 7.4.

7.6.4 Hypotheses

It was predicted that germination would fail on the untreated tailings due to the extreme acidity of the medium and its associated impact on the solubility of phytotoxic metals. The addition of lime to the tailings was predicted to improve germinating and growing conditions in the tailings. The tailings treated with the low and moderate (8.25 & 16.5

Mg/ha) rates of lime, however, were expected to reacidify due to the ongoing oxidation of remnant sulphide minerals. Plant die-back was therefore anticipated on these treatments during the course of the trial. The addition of lime at a rate equivalent to 112 Mg/ha was predicted to prevent reacidification of the tailings and to facilitate plant growth throughout the growing period. This very high rate of lime, however, was predicted to detrimentally affect the growth of the various plants due to alkaline induced nutrient deficiencies.

The metal-tolerant plant varieties were predicted to out-yield the non-tolerant varieties on the low and moderate lime treatments due to their greater tolerance of heavy-metals. The rationale was that under acidic conditions the bioavailability of phytotoxic metals generally increases.

7.6.5 Results

7.6.5.1 Germination

Since all plant species failed to germinate on the untreated tailings and the only taxa to germinate on the $\frac{1}{2}$ pH-6 treatment was *L.corniculatus*, the following discussion of germination trends relates to the 1 pH-6 and TAGP treatments that received 16.5 and 112 Mg of lime per hectare respectively (Table 7.8). The probable causes of complete germination failure on those pots that received ≤ 8.25 Mg lime/ha are discussed in section 7.6.5.2.

Over the four week period that seed germination was monitored, marked variability in germination trends amongst the species was evident (Figure 7.4). Very little variation, however, was noted between the metal-tolerant and non-metal-tolerant cultivars of the two grass species investigated (*F.rubra* and *A.capillaris*). Seed germination of both varieties of *F.rubra* peaked at week 2, with average germination rates of 50 - 60 % being attained. Survival rates of *F.rubra* were high with less than 10% of the plants dying during the monitoring period (Figure 7.4). Similar germination trends were observed for *L.corniculatus*, although slightly lower germination rates of approximately 40% were attained. Lime application rates had little effect on the germination rates of *L.corniculatus* and *F.rubra*, although a slight drop in germination was noted for

L.corniculatus at the highest liming rate. Slightly higher seedling mortality was also noted for *L.corniculatus* at the TAGP liming rate (Figure 7.4 b).

At the 1 pH-6 liming rate germination rates of close to 100% were attained for both varieties of *A.capillaris* within a week of sowing. The survival rate of the seedlings, however, was low, with only about 50% of the Parys Mountain seedlings and 36% of the Egmont seedlings surviving through to week 4 of the trial (Figure 7.4a). *A.capillaris* germination rates of approximately 80% were attained in the TAGP treatments indicating a notable deterioration in germination conditions to those found at the lower liming rate (Figure 7.4b).

7.6.5.2 Yield Response

(i) Nil Lime Treatment

As predicted, seed germination on the nil lime treatment failed. The pH of the untreated tailings was found to remain extremely low and relatively constant throughout the duration of the trial, dropping only slightly over the 11 week trial period from a pre-incubation level of 2.29 in the control pots to about 2.13. Similar pH values of 2.19 ± 0.02 were found in the trial pots which were analysed at the end of the 8 week growing period. As discussed in section 7.5.1, the pH of the control pots was monitored for a further 3 months after the final herbage cut was made. Measurements of pH made at the end of this period indicate that the pH of the non-limed control pot rose slightly despite what were believed to be near optimal conditions for biochemical sulphide oxidation (Figure 7.5).

The lack of a substantial decrease in the pH of the unamended tailings suggests that a buffering system exists in the Tui Mine tailings at low pH. This finding is consistent with other research that has found that below pH values of about 3.5, pH buffering in acid sulphate soils, pyritic tailings and spoil occurs due to the acid hydrolysis of aluminosilicate clays, jarosite and silica (Miller, 1979; Dent, 1986). All oxides, carbonates and silicates are generally alkaline in reaction (Mengel & Kirkby, 1987). The hydrolysis of these minerals serves to buffer pH change and generally prevents the pH of sulphide-bearing materials falling below 1.5 even under moist, non-leaching conditions (Dent, 1986).

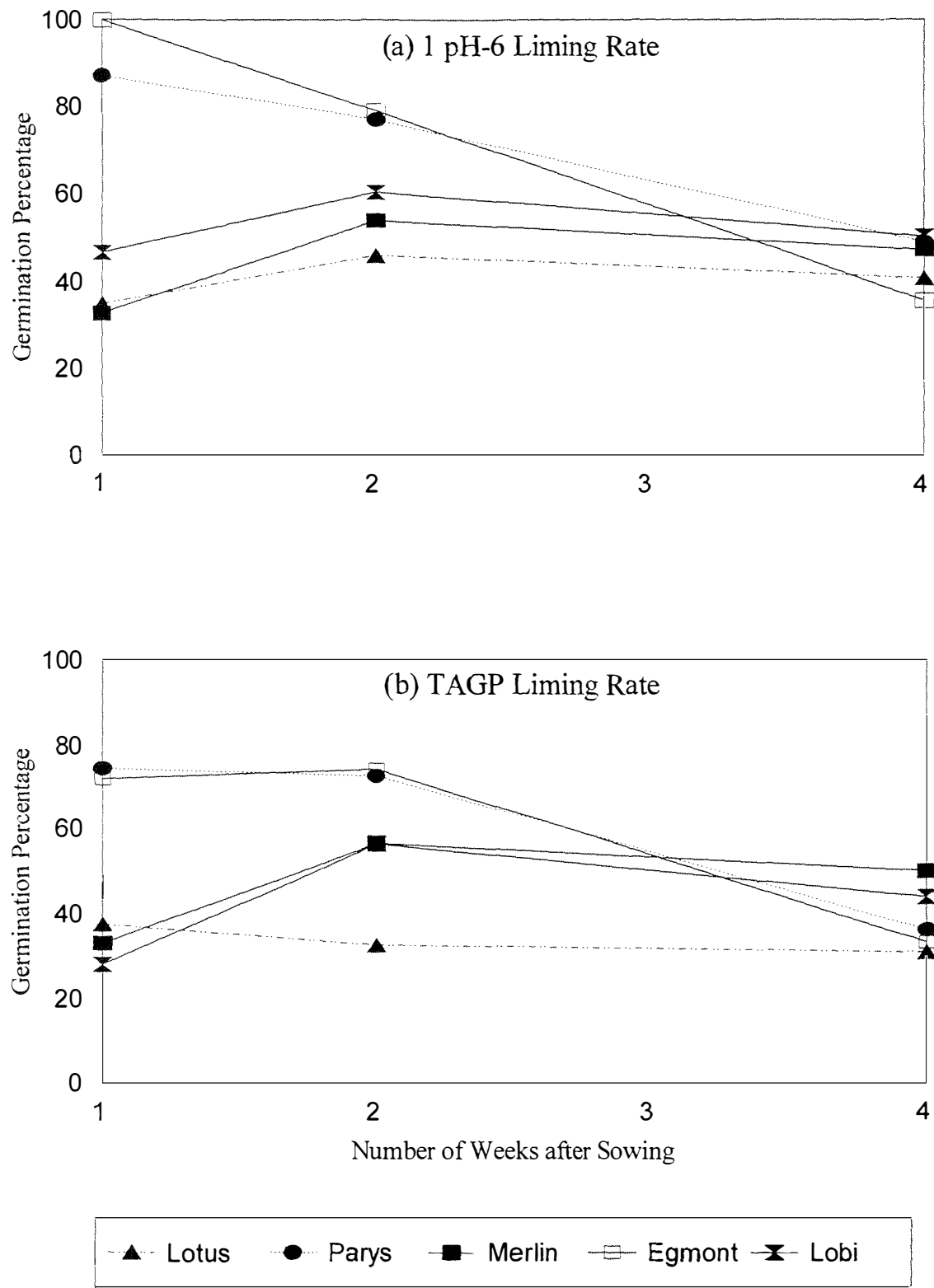


Figure 7.4 Percentage germination at various periods after sowing at (a) 1 pH-6 liming rates and (b) TAGP liming rates. All plant taxa failed to germinate on the nil and ½ pH-6 lime treatments.

Germination failure of all taxa on the untreated tailings was not unexpected given the extremely acidic nature of the medium and total lack of vegetation on the Tui mine site. Plant mortality and germination failure at low pH (< 4.0) is generally attributed to phytotoxicity associated with high hydrogen ion activity and/or the release of toxic metal cations (eg. Al^{3+} or Cu^{2+}) into the soil solution (Gemmell, 1977; Mengel & Kirkby, 1987). At low pH enzyme inactivation is considered to be one of the primary mechanisms leading to toxicity. Soil pH values of 3.5 or less are known to inactivate many vital enzyme systems bringing about inhibition of root respiration and restricting the uptake of mineral salts and water (Gemmell, 1977). Among the biological processes most effected by metals are the mineralisation of N and P, the degradation of cellulose and possible N fixation (Förstner, 1991). At low pH levels cell membranes may also become dysfunctional and 'leak' plant nutrients (particularly K^+) out of the root cells into the soil solution (Mengel & Kirkby, 1987). This leakage effect is generally counterbalanced by Ca^{2+} addition.

Because divalent transition metals readily react with the amino, imino and sulphydryl groups of proteins, plant enzyme inactivation is a particular problem at low pH due to the increased activity of metal cations. Previous research also indicates that some metals may also damage cells by acting as anti-metabolites or by forming precipitates or chelates with essential metabolites (Nriagu, 1984).

At low pH, the bioavailability of Ca, P and Mo is generally low. Research indicates that the accumulation of Al on root surfaces can inhibit the uptake of these plant nutrients (Enright, 1984). Although nutrient availability is not generally considered critical to germination, macro and micronutrient deficiencies can seriously impact the growth pattern of establishing seedlings. Phosphorus (P) deficiency is one of the most commonly observed nutrient deficiencies at low pH and poses a major problem to establishing plants in conditions where acidity is sufficiently low not to be directly toxic to plant roots (Mengel & Kirkby, 1987).

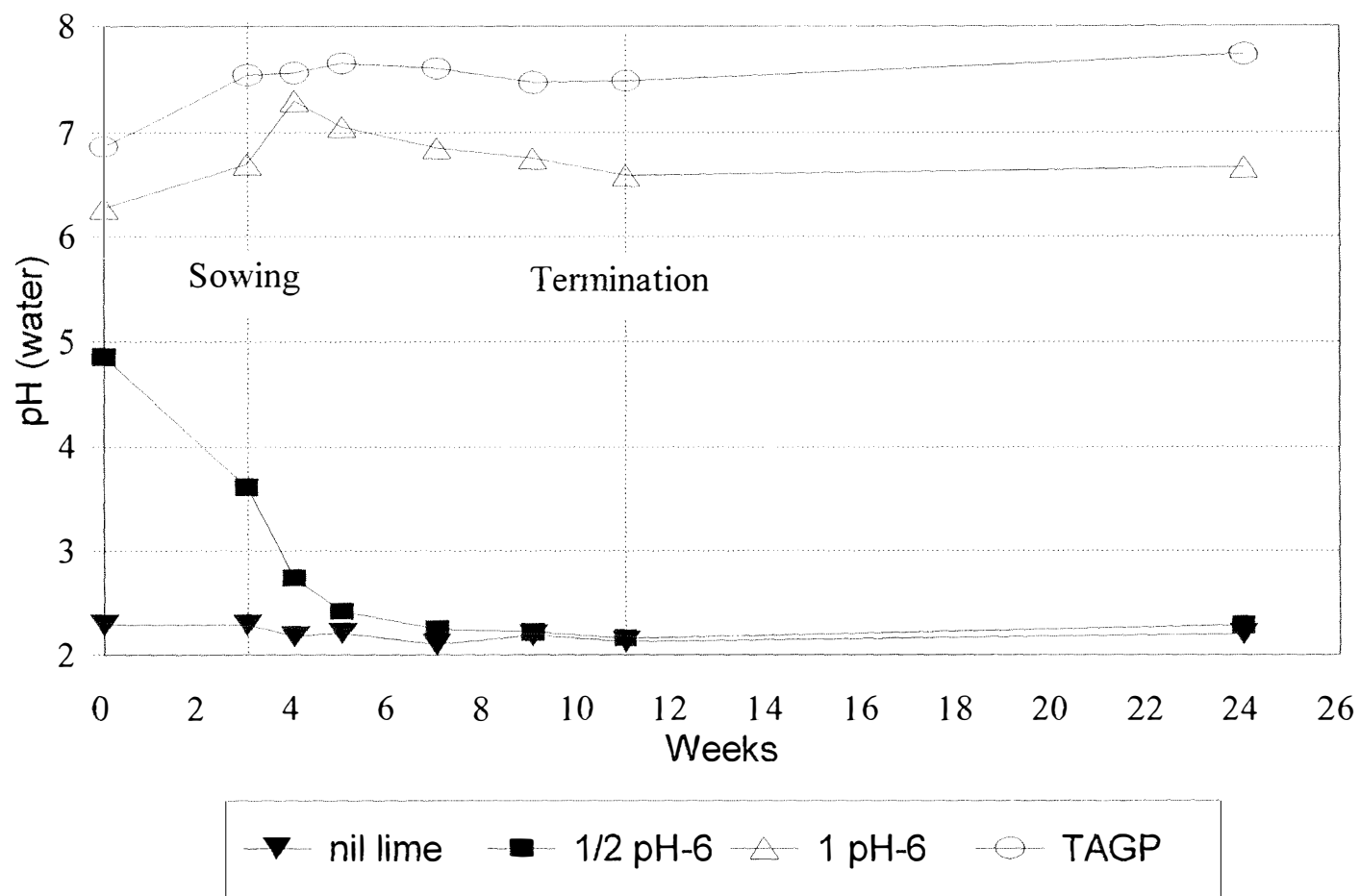


Figure 7.5 Changing pH of non-sown 'control pots' treated with various rates of lime.
 (Where nil = 0 Mg/ha, 1/2 pH-6 = 8.25 Mg/ha, 1 pH-6 = 16.5 Mg/ha, TAGP = 112 Mg/ha)

Whilst analysis of the tailings sampled from the unamended control pot at week 11 (day 56) of the trial indicated that both Olsen P⁵ and total P concentrations were very low in the tailings (Table 7.9), the low P status of the nil treatment is not likely to have effected seed germination because seeds generally contain adequate nutrient reserves to meet germination requirements.

Table 7.9 Soil fertility parameters of Trial One control pots determined at sowing (Week 3) and at the end of the growing period (Week 11). Medium values for New Zealand soils are based on the data of Blakemore *et al.* (1987). *Values are expressed as mg/kg. † Values expressed as meq/100g .
— indicates that CEC values could not be determined. nd = not determined

Soil Parameter	Medium Values	nil		½ pH-6		1 pH-6		TAGP	
		Week 3	Week 11	Week 3	Week 11	Week 3	Week 11	Week 3	Week 11
pH _(water)	5.3-6.5	2.29	2.13	3.62	2.16	6.70	6.59	7.55	7.49
Olsen P*	20-30	3.4	0.8	2.4	0.8	4.1	2.0	3.1	1.2
Total P*	400-800	nd	77	nd	58	nd	65	nd	65
Total N*	3000-6000	nd	13	nd	13	nd	13	nd	13
Sulphate*	15-50	1230	2505	1215	2756	1695	1608	1530	3568
Exch. Ca [†]	5.0-10.0	0.5	0.6	6.9	5.4	12.5	12.0	65.2	56.4
Exch. K [†]	0.5-0.8	0.01	0.09	0.01	0.09	0.03	0.12	0.02	0.13
Exch. Na [†]	0.3-0.7	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2
Exch. Mg [†]	1.0-3.0	0.13	0.11	0.10	0.10	0.16	0.10	0.35	2.83
CEC [†]	12-25	15	23	12	27	—	13	—	—

Aluminium toxicity is likely to have detrimentally effected seed germination in the nil treatment and is recognised as a serious problem affecting many acidic soils and mining wastes (Enright, 1984). Several methods have been developed to measure available soil Al. The critical level at which Al becomes toxic to plants varies from method to method and appears to be dependent not only on the plant species but also on the soils' organic matter content, P status and electrolyte content (Edmeades *et al.*, 1983). The presence of even small concentrations of Al³⁺ and monomeric Al species such as Al(OH)²⁺ and Al(OH)₂⁺ in the soil solution has been shown to seriously affect plant growth, particularly root growth (Enright, 1984; Mackay *et al.*, 1991). Mengel & Kirkby (1987) outlined one study in which soil Al³⁺ solution concentrations as low as 1.1×10^{-5} M caused considerable root damage to certain species. Aluminium absorbed into the root

⁵ See method of Olsen *et al.*, 1954

system is believed to affect root cell division by interfering with genetic mitosis in the growing points (Enright, 1984). Roots effected by excessive Al concentrations are characterised by the growth of close lateral branches and the lack of fine branches and roots hairs.

Research conducted in New Zealand investigating the influence of Al availability on the growth of white clover (*Trifolium repens*) indicates that soil Al concentrations (0.02 CaCl₂ extractable) in excess of about 3 mg/kg are potentially toxic to plants (Edmeades *et al.*, 1983; Hume *et al.*, 1988). In addition, Edmeades *et al.* (1983) found that Al toxicity in white clover generally occurs below pH(H₂O) 4.7 and when 1M KCl extractable Al concentrations exceed 1.0-2.0 meq/100g. Hume *et al.* (1988) observed that plant tolerance of Al varied from soil to soil and that a significant proportion of the soluble Al as measured by 0.02 CaCl₂ was complexing with soil organic matter in the extractant. The organically bound Al was found to be less harmful to plants than the non-organically bound forms, explaining the apparent tolerance of plants to comparatively high levels of extractable Al in some soils. The findings of Hume *et al.* (1988) are consistent with those of other studies (Bartlett & Riego, 1972; Kapland & Estes, 1985; Shuk-Ching & McColl, 1990; Gurung *et al.*, 1996) and are pertinent to the plant trials discussed in this chapter because of the inherently low organic matter content of the Tui Mine tailings. Analysis of the tailings indicate they contain just 0.06 % total organic carbon and 14 mg/kg dissolved organic carbon (Baskaran *et al.*, 1996). Thus, for all intents and purposes the Tui mine tailings contain negligible organic matter and have little capacity for organically complexing potentially harmful Al compounds.

Since phytotoxic monomeric Al compounds are absorbed non-specifically at negatively charged sites on clay minerals, the presence of such minerals can play a similar role to that of organic matter in complexing Al. This adsorption, however, is pH dependent and becomes weaker as the pH falls. Under acid conditions, H⁺ is adsorbed by exposed Al-OH groups on the edge of clay minerals, weakening the Al-O bond which can ultimately result in the liberation of Al as discrete ions. Subsequent hydrolysis of the Al renders the Al readily available for plant uptake.

Although ICP analysis indicated that the total concentration of Al in the tailings was comparatively low compared to concentrations typically found in soils (Table 7.1), elevated concentrations of 1M KCl and 0.02M CaCl₂ extractable Al concentrations were found in the unamended tailings (Figure 7.6). The two extraction procedures used were found to extract almost identical concentrations of Al and clearly indicate that the tailings contain potentially phytotoxic concentrations of Al. On day 28 of the trial, for example, the concentration of 0.02M CaCl₂ extractable Al in the unamended control pot was over 100 times the critical level associated with poor white clover growth (Edmeades *et al.*, 1983; Hume *et al.*, 1988). The potential impact of the high concentrations of readily available Al on seed germination was undoubtedly exacerbated by the very low organic matter content and low clay content of the untreated tailings. In a study investigating Al toxicity problems associated with mine wastes, Enright (1984) found that the most effective treatment to reduce toxicity was to apply lime (2000 kg/ha) in combination with superphosphate (200 kg/ha).

Although toxic concentrations of Mn are often found in association with high concentrations of Al, 0.02M CaCl₂ extractable Mn concentrations were very low (< 6 mg/kg) in the tailings due to their inherently very low Mn content (Table 7.1). Previous research indicates that critical toxic 0.02M CaCl₂ extractable Mn concentrations lie between 550 and 650 mg/kg (Andrew & Hegarty, 1969; Smith *et al.*, 1983). Based on this evidence it is apparent that Mn toxicity is not inhibiting germination or growth of plants on the tailings.

Other metals, however, were present in concentrations postulated to be sufficiently high to affect germination on the non-lime treated tailings. These metals included Cu, Fe and Zn (Figure 7.6). Despite the extremely high total Pb content of the tailings (13885 mg/kg), analysis of the tailings indicate that the vast majority of this Pb is insoluble and not readily available to plants. At each temporal sampling, 0.02M CaCl₂ extractable Pb concentrations were in the vicinity of just 10 mg/kg (Figure 7.6). Although the weak acid extractant (0.1M HCl) was found to extract more Pb than the 0.02M CaCl₂ extractant, the amount extracted was only a very small proportion of the total concentrations of Pb present in the tailings (Figure 7.6). The failure of these two extractants to liberate significant quantities of Pb into solution is consistent with finding

of previous research which indicates that Pb is generally found in very small concentrations in soil solutions due to its tendency to form highly insoluble compounds (eg. PbSO_4 and PbCO_3) and to combine with hydrous oxides and organic matter to form stable complexes (Shaw *et al.*, 1984; Davies, 1995). Research outlined by Davies (1995) investigating the solubility of Pb in highly contaminated soils (1890 - 49900 mg/kg) indicates that the proportion of the total Pb content represented by the soil solution ranges from 0.005% to 0.13%. The ability of many plant species to precipitate Pb compounds at the root cell walls and to prevent the translocation of Pb to sensitive shoot tissues further reduces the toxicity of this metal (section 3.7.5.2). Thus total Pb concentrations in 'soils' are generally accepted to be a poor indication of the potential toxicity of this element to plants (Davies, 1995).

Based on the findings of the trial and the preceding discussion, it is evident that a multitude of factors are likely to have contributed to germination failure on the nil treatment. Among those factors that are postulated to have been most detrimental to germination are the very high concentrations of Al, Cu, Fe, Zn and H^+ that prevailed in the soil solution. Total germination failure in the nil treatment indicates that the unamended tailings provide an unsuitable germination environment and that the seeds' enzymal processes were inhibited soon after sowing, presumably due to the absorption of metal-contaminated soil water.

(ii) ½ pH-6 Treatment

On this treatment, four out of the five plant taxa failed to germinate despite the addition of the equivalent to over 8 Mg of CaCO_3 per hectare. By the end of the 3 week incubation period and prior to sowing the pH of the ½ pH-6 lime treatment had dropped from an initial pH (after liming) of about 4.9 to 3.6 (Figure 7.5). In spite of the extremely acidic conditions, about 5% of the *Lotus corniculatus* seed germinated on this treatment. None of the seedlings, however, survived more than a few days in the hostile growing conditions.

During the course of the pot trial the pH of the tailings in the control pot continued to decrease to the point where at week 9 there was no significant difference between the pH of the ½ pH-6 lime treatment and the nil lime treatment (Figure 7.5). This rapid drop

in pH demonstrated the inability of the tailings to buffer pH change and the extremely reactive nature of the tailings under near optimum conditions for sulphide oxidation. Previous research conducted on colliery spoils suggests that no significant buffering systems exist between pH 6.5 and 3.5 (Wiggering, 1993). As previously discussed, however, pH buffering is likely to occur below pH 3.5 in pyritic tailings and spoil (Miller, 1979; Dent, 1986). The rapid drop in pH followed by relatively constant pH is thus believed to reflect the neutralisation and the eventual exhaustion of the added calcium carbonate by acid produced via remnant sulphide oxidation and the hydrolysis of jarosite, followed by pH buffering of the material by acid hydrolysis of silicate minerals and oxides constituting the tailings.

Comparison of Figures 7.6 (nil lime) & 7.7 indicates that the addition of lime at a the $\frac{1}{2}$ pH-6 rate (8.25 Mg/ha) resulted in the initial reduction of most metal concentrations in the tailings and improved germination conditions. Inspection of the concentration data at day 28 of the trial (4 weeks after sowing), however, revealed that the addition of this relatively low rate of lime resulted in treble the amount of Cu, Fe and Zn being extracted by 0.02M CaCl₂. Arsenic concentrations also increased from about 3 mg/kg to over 7 mg/kg. The concentrations of 1M KCl extractable Al and 0.1M HCl extractable Cu, Fe and Zn were similarly found to increase in the $\frac{1}{2}$ pH-6 treatments.

The comparatively higher ‘extractability’ of some metals resulting from the application of this relatively low rate of lime is clearly evident in Figures 7.11 & 7.12. The metal concentration trends observed in these figures are consistent with the findings of the lime incubation (Chapter 6) and further suggests that the applications of low rates of lime to the Tui Mine tailings may actually enhance sulphide oxidation and exacerbate acid mine drainage⁶. This finding is extremely important in that it has far reaching implications for amendment strategies.

Clearly any attempts to revegetate the tailings through the application of lime must ensure that sufficient is added to eliminate the ‘catalytic’ effect that low liming rates appear to have on sulphide oxidation within the Tui tailings. Whilst the catalytic effect

⁶ A similar effect was noted in Trial Two (section 7.7) where the application of sludge at a rate of 110 Mg/ha was found to actually increase the availability of some metals in the amended tailings.

of carbonate has been noted before (Burt & Caruccio, 1986), it appears it that there are few references to this potential problem elsewhere within relevant literature. Burt & Caruccio

(1986) reported that the addition of carbonate material below a critical “*alkalinity threshold level*” slightly raises the materials pH, which facilitates the more rapid oxidation of ferrous iron. This in turn was found to accelerate the oxidation of pyrite. Possible mechanisms explaining the ‘catalytic’ effect of low rates of lime are further discussed in the lime incubation experiment reported in Chapter 6 where similar results were observed.

Germination failure almost on a par with that observed in the untreated tailings is again attributed to the extremely low pH of the ½ pH tailings which culminated in the high availability of H⁺ and several potentially phytotoxic metal ions in the soil solution. The concentrations of Al, Fe and Cu were again particularly high and are likely to have been largely responsible for germination failure.

Although the failure of 8.25 Mg/ha lime to sustain the pH of the tailings at a level conducive to seed germination was a significant finding in itself, the result was in some respects disappointing in that it prevented an assessment of the various plant taxa to be made under moderately acidic growing conditions. The comparatively high levels of dry matter produced by metal-tolerant *F.rubra* (Merlin) grown on substantially more acidic treatments (pH 4-5) in Trial Two (Figure 7.15) indicates that the pH (6.5-7.0) induced by the 1 pH-6 liming rate may have been far from optimal in terms of plant growth. Based on this observation it is likely that improved plant yields would have been attained from the application of an intermediate liming rate between 8.25 and 16.5 Mg/ha. The success of such a rate would clearly depend on its ability to prevent long term reacidification of the tailings.

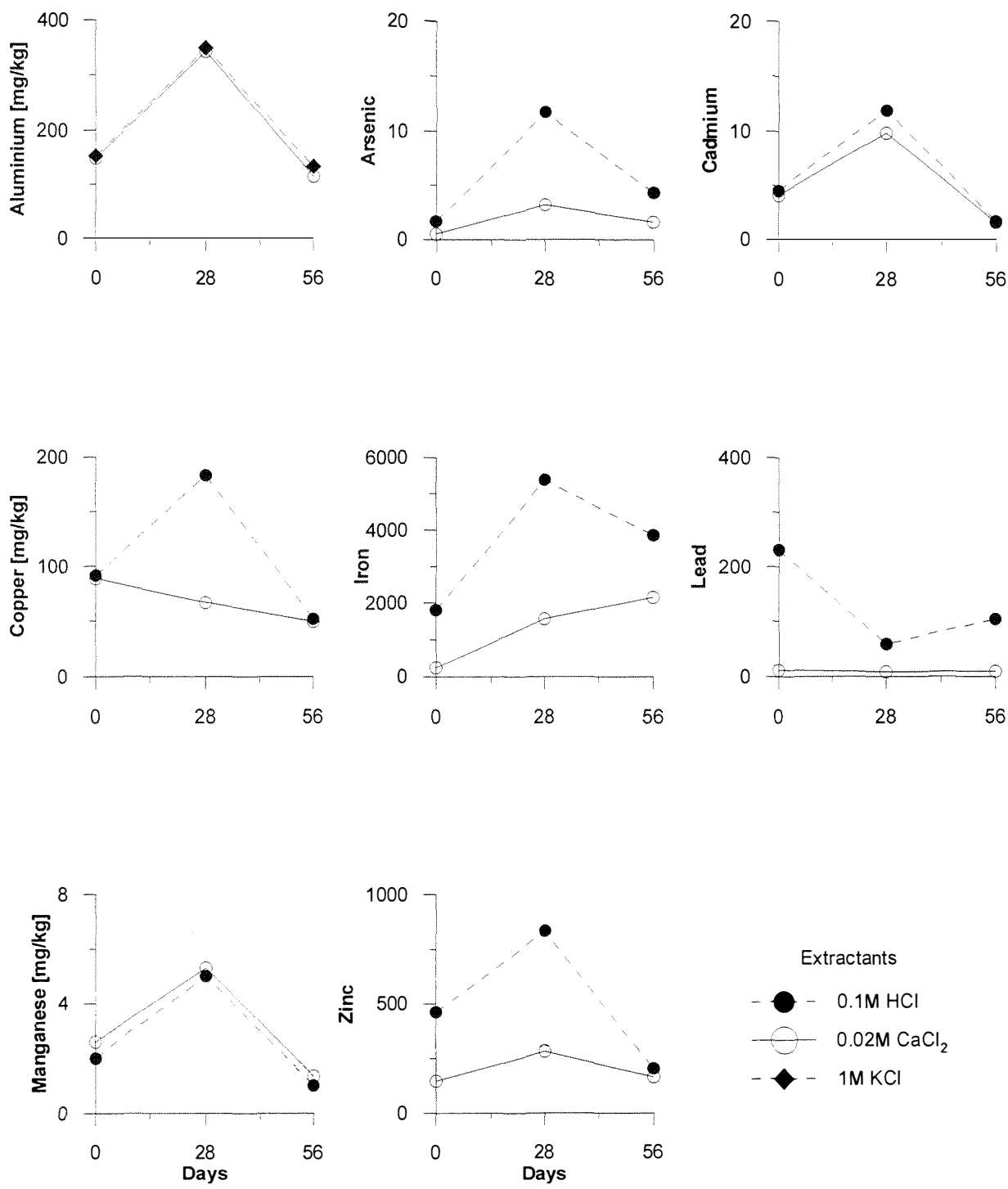


Figure 7.6 Changes in metal concentrations as extracted by 0.1M HCl (●), 0.02M CaCl₂ (○) and 1M KCl (◆) for nil lime treatment during the growing period.

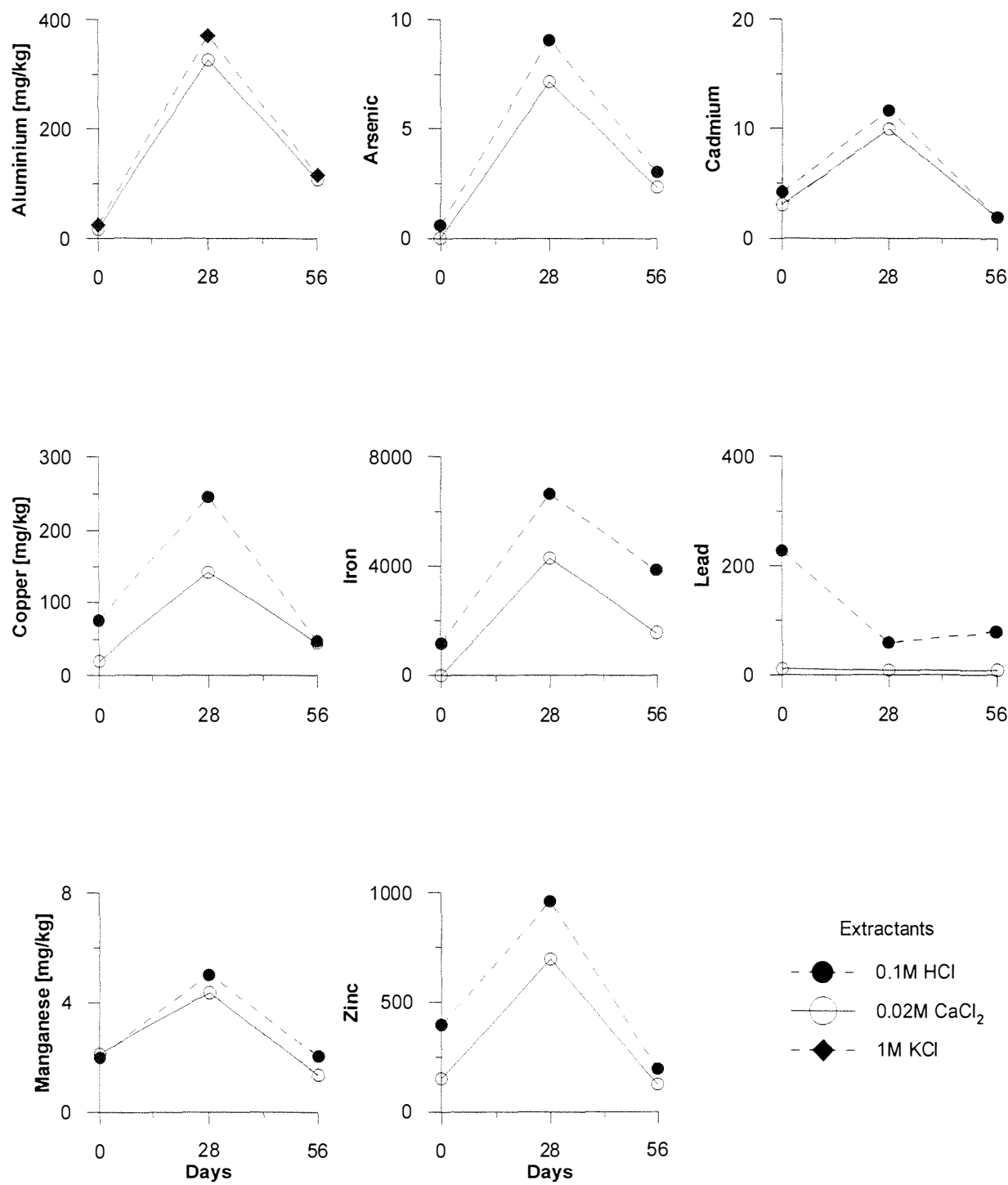


Figure 7.7 Changes in metal concentrations as extracted by 0.1 M HCl (●), 0.02 M CaCl₂ (○), and 1 M KCl (◆) for $\frac{1}{2}$ pH-6 lime treated tailings during the growing period.

(iii) 1 pH-6 Treatment

In contrast to the nil and ½ pH-6 liming rates, 'satisfactory' germination and subsequent seedling growth was achieved on the two highest liming rates, particularly at the 1 pH-6 rate (16.5 Mg CaCO₃/ha). On this treatment the metal-tolerant varieties of *Agrostis capillaris* (Parys Mountain) and *Festuca rubra* (Merlin) were found to significantly out-yield their non-metal-tolerant counterparts with the metal-tolerant variety of *A. capillaris* out-yielding the non-metal-tolerant variety by more than 10 times (Figure 7.8; Plate 7.2). Merlin, the metal-tolerant variety of *F. rubra* out-yielded the non-metal-tolerant variety Lobi by about 4 to 1 (Plate 7.3) and proved the most successful of the plant taxa yielding an average of 0.92 g and 0.44g of dry matter per pot at the 1 pH-6 liming rate and TAGP liming rates, respectively (Figure 7.8) .

Although the dry matter yields of *Lotus corniculatus* were comparable to those of the non-metal-tolerant grass species on the 1 pH-6 treatments, the overall performance of this taxa was poor (Figure 7.8). The plant shoots were stunted and had developed symptoms of chlorosis consistent with that of N deficiency (Plate 7.4). Although significantly ($P < 0.05$) higher yields of *L. corniculatus* were obtained from the pots inoculated with Rhizobium at the 1 pH-6 liming rate, analysis of variance indicates that the overall effect of Rhizobial inoculation on yields in the trial was non-significant ($P = 0.167$). The lack of any significant positive effect of inoculation on yield is clearly demonstrated by the reversal of the yield trend at the higher (TAGP) liming rate. Analysis of variance did, however, identify a significant ($P < 0.05$) interaction between lime and rhizobial inoculation in relation to dry matter yield. This interaction, however, is questionable because at the end of the growing period the root systems of selected *L. corniculatus* plants from both lime treatments failed to show any evidence of rhizobial nodulation. The morphology of the root systems were, however, abnormal and characterised by short, over-thickened lateral and primary roots. The lateral roots were generally only a few millimetres long and largely devoid of fibrous roots. Although these effects are characteristic of Al they are also commonly associated with various heavy metal toxicities and some nutrient deficiencies (Mengel & Kirkby, 1987; MacLean *et al.*, 1992).

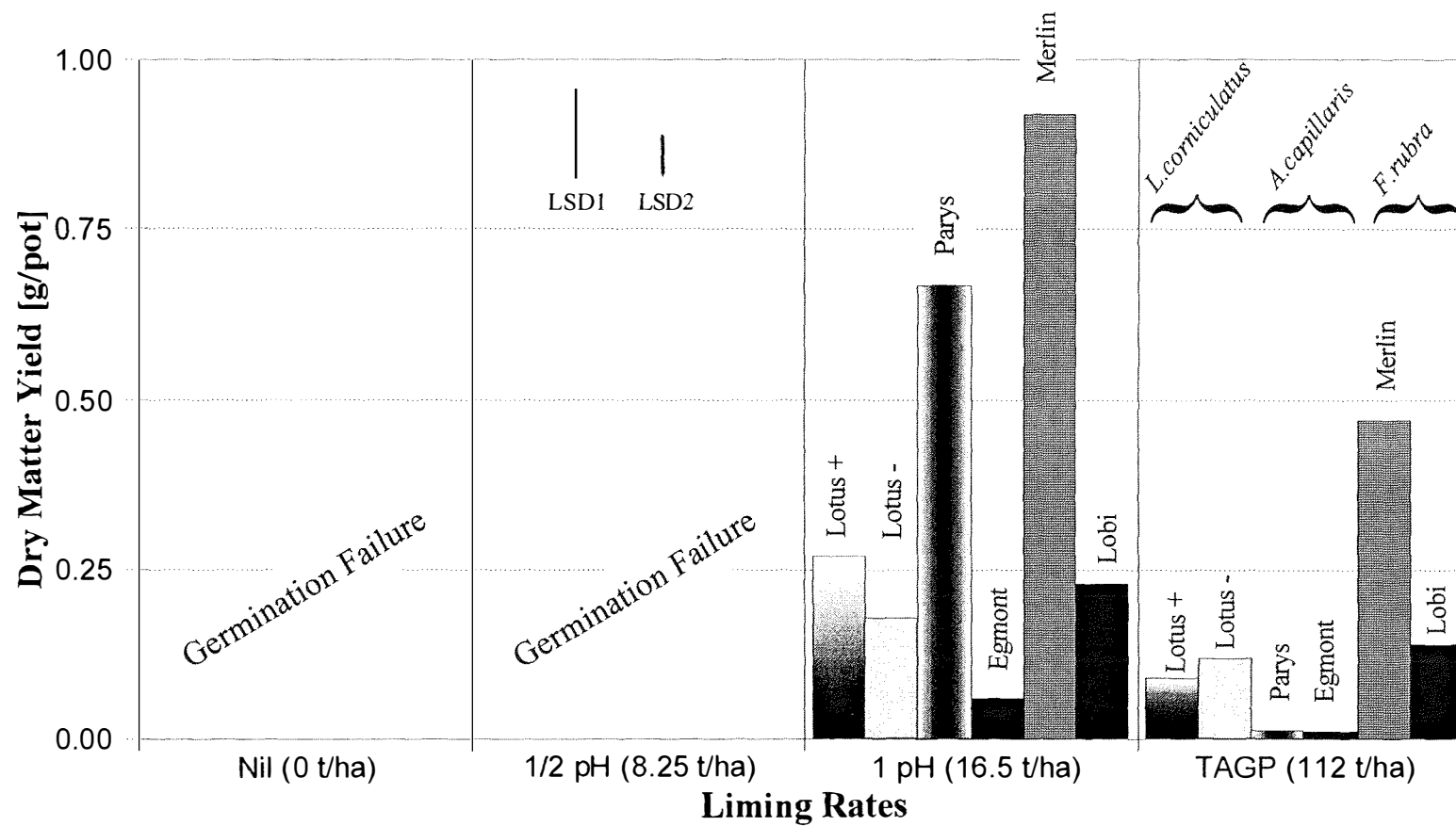


Figure 7.8 Dry matter yields of different plant taxa at various liming rates. LSD1 = least significant difference for non-leguminous plants (5%) ; LSD2 = least significant difference for *L. corniculatus* only (5%).

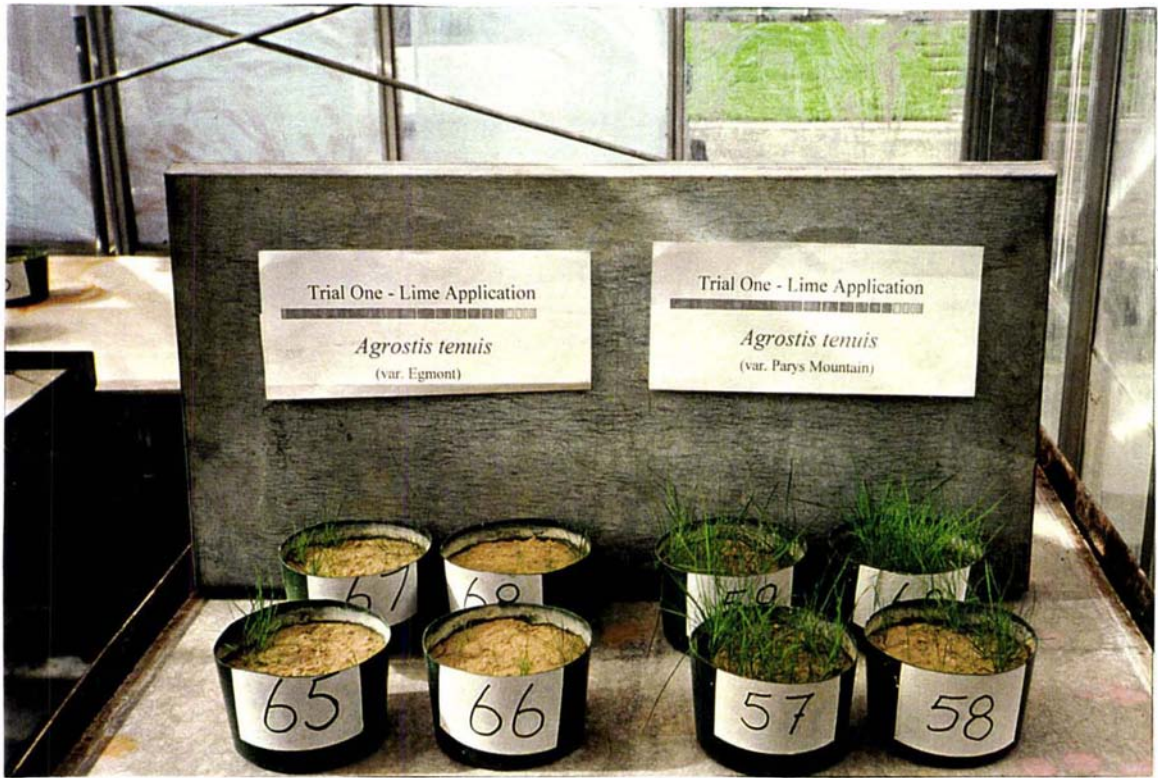


Plate 7.2 This photograph which was taken about 8 weeks after sowing compares the growth of two cultivars of *Agrostis capillaris* (*tenuis*) on tailings amended with a rate of lime equivalent to 16.5 Mg/ha (1 pH-6 rate). The metal-tolerant cultivar (Parys Mountain) located on the right-hand-side of the plate was found to out-yield the non -metal-tolerant cultivar (Egmont) by a factor of more than 10.



Plate 7.3 This photograph compares the growth of two varieties of *Festuca rubra* grown on tailings amended with 16.5 Mg CaCO₃ (1 pH-6 rate) 8 weeks after sowing. The metal-tolerant variety (Merlin) on the right-hand-side of the plate was found to produce about 4 times more dry matter than the non-metal-tolerant cultivar (Lobi).

The ability of high rates of lime to substantially increase the pH of the tailings and to simultaneously reduce the solubility of potentially toxic metals appears to be the primary reason why most of the seeds successfully germinated and grew on the 1 pH-6 and TAGP lime treatments (Figures 7.9 & 7.10). The application of lime at the 1 pH-6 rate was found to increase pH of the tailings to the desired pH of about 6. During the 3 week incubation period, however, the pH continued to rise and by week 4 of the trial (1 week after sowing) the pH peaked at approximately 7.3 (Figure 7.5). By the end of the growing term the pH had dropped to about 6.6 where it remained for the duration of the monitoring period (up until week 24). The pH of the planted pots (6.60 ± 0.13) measured at week 11 of the trial were found to compare very well with the pH observed in the control pot (6.59).

With the exception of Pb, the concentrations of metals extracted by 0.02M CaCl₂ were all found to decrease considerably within those treatments receiving either of the two higher rates of lime (Figures 7.9 & 7.10). If day 28 of the trial is used to compare 0.02M CaCl₂ metal concentrations between treatments, it is evident that those elements to demonstrate the most substantial decrease in concentration were Al, As, Cu, Fe and Zn (Figure 7.11). Calcium chloride (0.02M) extractable Al concentrations in the 1 pH-6 and TAGP treatments were reduced from 343 mg/kg in the nil treatment to about 8 and 1 mg/kg, respectively.

Copper concentrations that were in the vicinity of 48 mg/kg in the nil treatment and 140 mg/kg in the ½ pH-6 treatment were reduced to less than 0.5 mg/kg in both 1 pH-6 and TAGP treatments. Similarly, Zn concentrations were reduced from about 280 and 695 mg/kg in the nil and ½ pH-6 treatments to about 27 and 2 mg/kg. Of all the metals monitored, however, Fe was found to demonstrate the most spectacular decrease in concentration, dropping from over 1500 mg/kg in the nil treatment and 4200 mg/kg in the ½ pH-6 treatment to less than 0.1 mg/kg in the tailings treated with the two higher rates of lime (Figure 7.11). In acid 'soils' high levels of soluble Fe can reduce plant growth either directly or through its affect on the uptake of other nutrients, such as P (McLaren & Cameron, 1996). Direct Fe toxicity is often found to occur in conjunction with K⁺ deficiency and is a problem often associated with rice production where soluble Fe levels in the soil solution may increase from 0.1 µg/ml to >50 µg/ml within a few

weeks of crop flooding (Mengel & Kirkby, 1987). Clearly the Fe concentrations encountered at the nil and ½ pH liming rates were extremely high and likely to have been directly toxic to most plant species.

Concentrations of 1M KCl Al and 0.1M HCl extractable As, Cu, Fe and Zn metal concentrations were also found to decrease markedly at the highest two liming rates, particularly at the TAGP rate (Figure 7.12). 0.1M HCl extractable Pb concentrations were reduced to 2 mg/kg or less at this rate, whereas lime application at the 1 pH-6 rate appeared to have little effect on the availability of 0.1M HCl extractable Pb concentrations (Figure 7.12). The neutralisation of 0.1M HCl with CaCO₃ potentially explains the relatively low quantities of metals extracted in the heavily limed tailings.



Plate 7.4 The *Lotus corniculatus* seen growing in this photograph (pots 53-55) are about 4 weeks old and are clearly performing poorly. Grown in tailings limed at a rate of 16.5 Mg/ha the plants showed signs of chlorosis and a generally yellow stunted appearance, symptoms consistent with N deficiency.

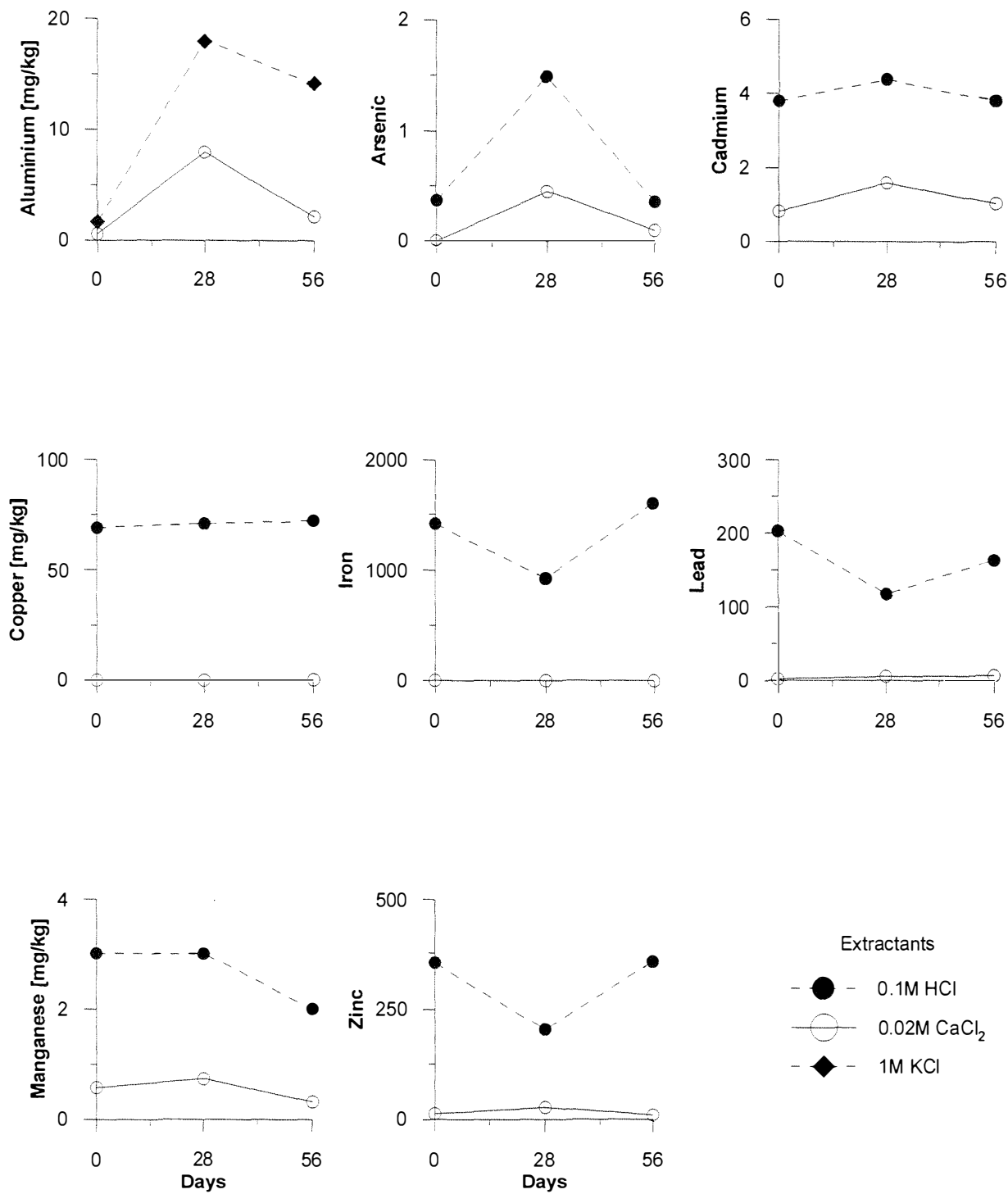


Figure 7.9 Changes in metal concentrations as extracted by 0.1M HCl (●), 0.02M CaCl₂ (○), and 1M KCl (◆) for 1 pH-6 lime treated tailings during the growing period.

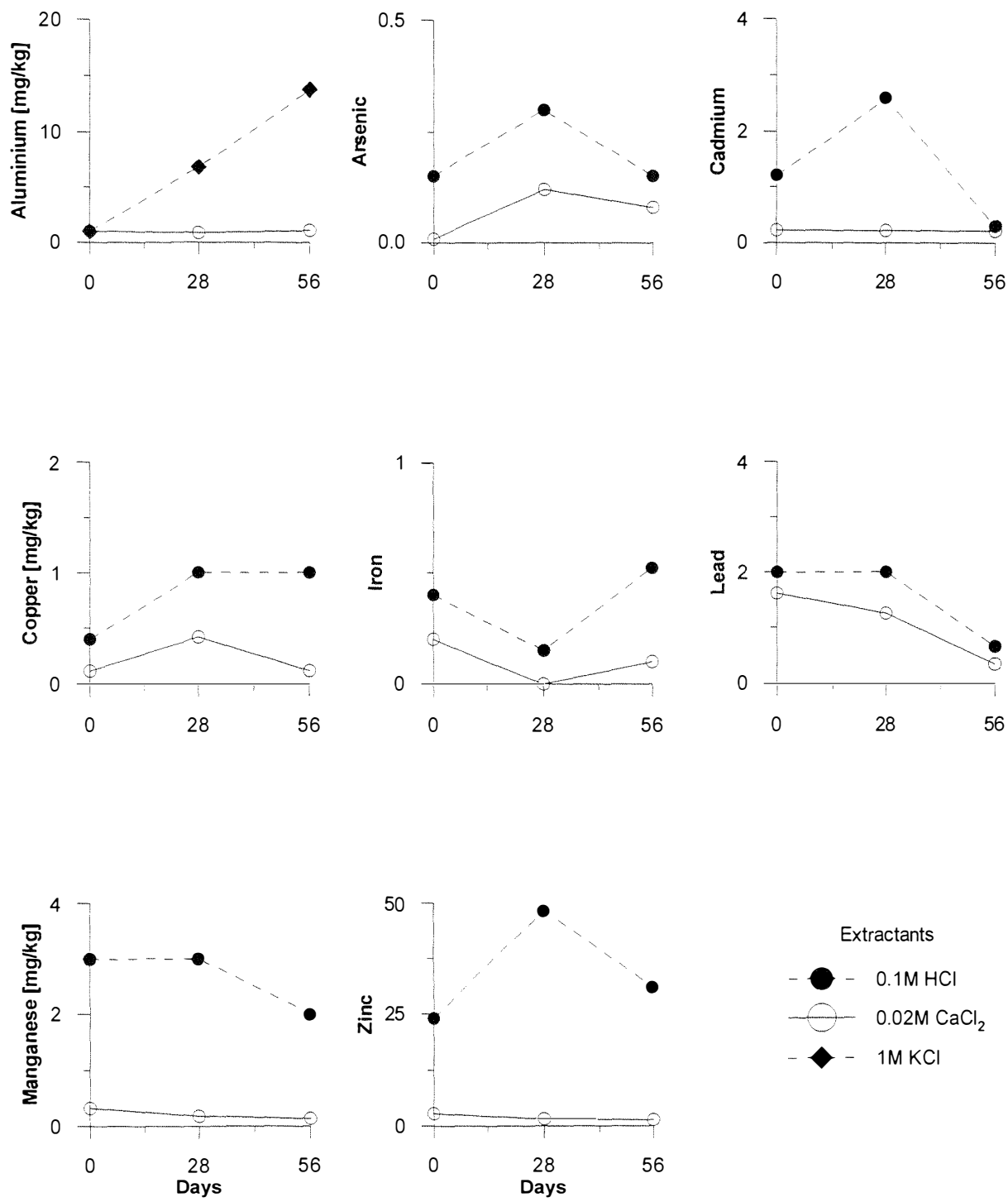


Figure 7.10 Changes in metal concentrations as extracted by 0.1M HCl (●), 0.02M CaCl₂ (○), and 1M KCl (◆) for TAGP lime treated tailings during the growing period.

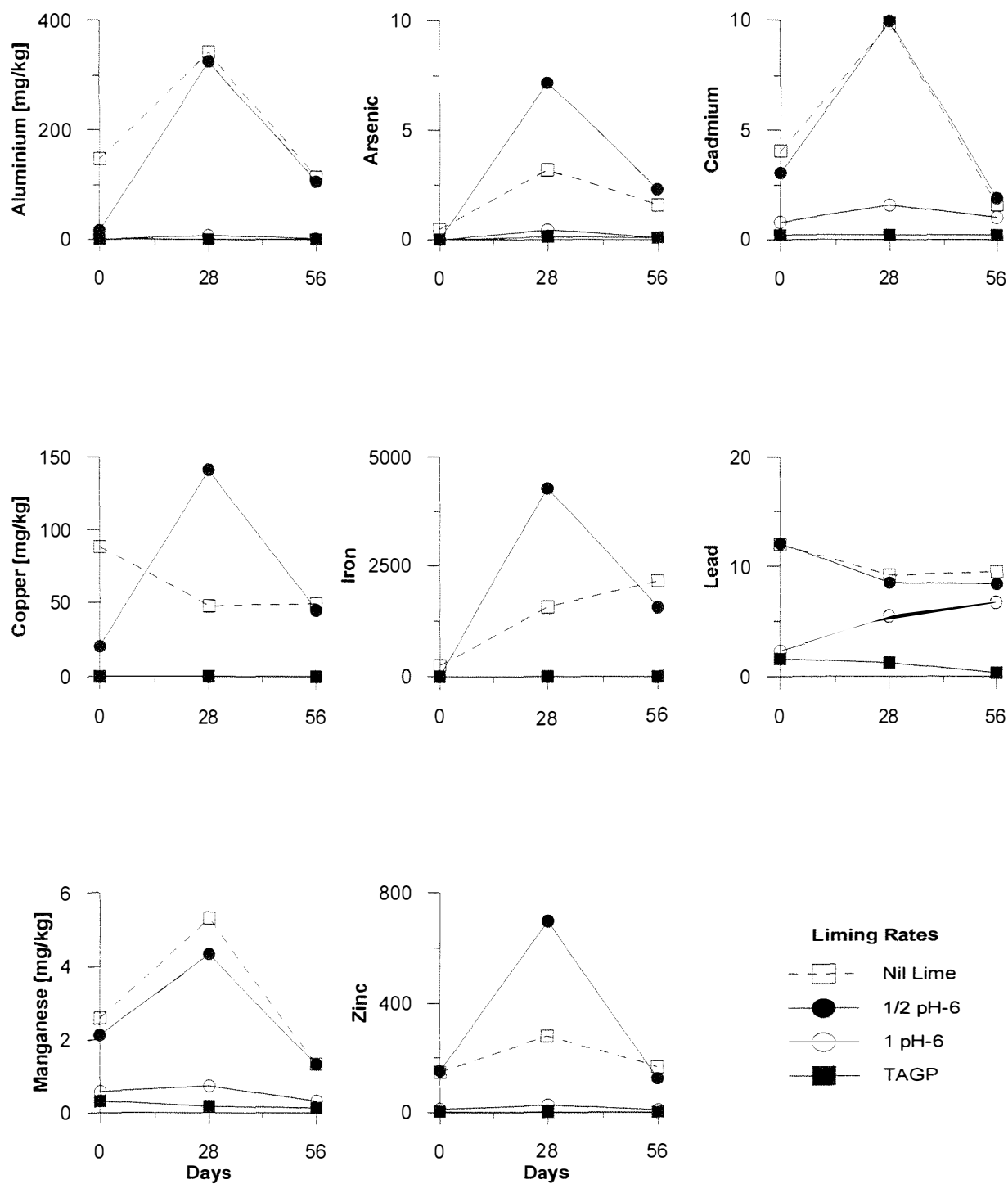


Figure 7.11 Concentrations of various metals extracted by 0.02M CaCl₂ at different lime rates.

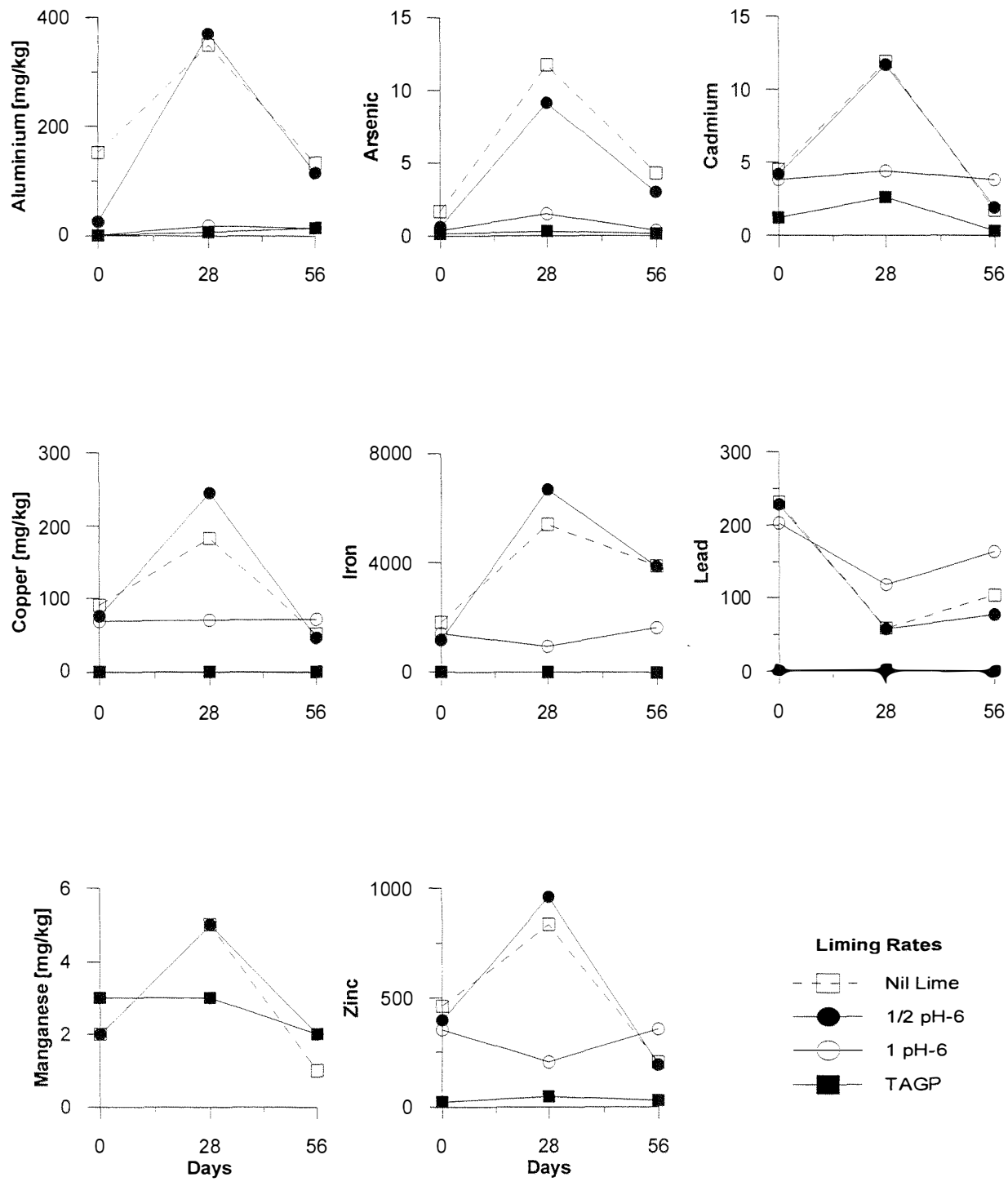


Figure 7.12 Concentrations of various metals extracted by 0.1M HCl and 1M KCl (aluminium only) at different liming rates.

(iv) TAGP Treatment

The pH of the control pot treated with 112 Mg/ha of lime (TAGP rate) was found to almost parallel that of the tailings treated with 16.5 Mg/ha of lime (Figure 7.5). The pH of the tailings was found to increase to about 7.5 by the end of the 3 week incubation period where it remained for the entire monitoring period. Comparison of the pH of the planted pots (7.59 ± 0.05) with that of the equivalent control pot (7.49) again indicated that there was good correlation between the control and trial pots and that the effect of plant growth on pH was minimal over the duration of the experiment.

Analysis of variance indicates that addition of the TAGP rate of lime had a negative and significant ($P < 0.001$) impact on plant yield. Inspection of Figure 7.8 shows that the average herbage yields of all five plant taxa decreased notably at the TAGP liming rate. The taxa demonstrating the greatest negative response to this rate of lime addition was the metal-tolerant variety of *A. capillaris* (Parys Mountain). Dry matter yields of this taxa decreased from nearly 0.7g per pot at the 1 pH-6 rate to about 0.01 g per pot at the higher liming rate (Figure 7.8).

Although the two effective liming rates had no significant effect ($P=0.328$) on the relative yields of *A. capillaris* and *F. rubra*, a highly significant ($P>0.001$) interaction was identified between lime treatment and plant metal tolerance. This interaction is readily observed in Figure 7.8 where at the highest liming rate (112 Mg/ha) a marked decrease in the relative performance of the metal-tolerant plants in relation to the non-metal-tolerant taxa is evident. This interaction is most marked for *A. capillaris* and suggests that the growth of this species is adversely affected by high alkalinity. In contrast to *A. capillaris*, no dramatic decrease in dry matter yields were noted for *F. rubra* at the TAGP liming rate and the metal-tolerant variety of *F. rubra* again significantly out-yielded the non-metal-tolerant variety by a ratio of more than 3 to 1. The reduction in yield of *F. rubra* var. Merlin at the higher liming rate was, however, significant ($P<0.05$).

Lime was also found to have a significant ($P<0.001$) and detrimental effect on the mean yields of *L. corniculatus*. At the TAGP rate yields of Lotus were only about 50% of that found at the 1 pH-6 rate (Figure 7.5). Lotus yields at the higher liming rate were

comparable to those of *F.rubra* var. Lobi but were significantly lower than those of the metal-tolerant variety of this species (Merlin). Although *L.corniculatus* treatments fared better than the two varieties of *A.capillaris*, the vigour and health of Lotus grown on the high lime treatment was poor. The morphology of the plants differed slightly to those grown at the 1 pH-6 rate in that they were generally more stunted in appearance and exhibited smaller foliage. The Lotus plants grown on the TAGP treatment again exhibited symptoms of chlorosis which suggests N deficiency may have adversely affected the growth of this species.

The 'satisfactory' performance of *F.rubra* var. Merlin on both the 1 pH-6 and TAGP lime treatments is believed to reflect the fact that this cultivar is a calcicole and is thus relatively well suited to the less acidic conditions induced by the two heavy liming rates. *A.capillaris* var. Parys Mountain in contrast is a calcifuge and thus prefers slightly acidic growing conditions (Johnson *et al.* 1977; Smith & Bradshaw, 1979; Bradshaw & Chadwick, 1980). The ability of *F.rubra* var. Merlin to yield comparatively high yields of dry matter on substrates of circumneutral pH is presumably related to mechanisms that this taxa has evolved to uptake nutrients that are generally unavailable to plants at this high pH. Such mechanisms combined with this taxa's tolerance to elevated concentrations of Pb and Zn are advantageous in that they eliminate competition and provide the plant with an ecological niche.

The decrease in relative yield differences between metal-tolerant and non-tolerant cultivars of the two respective grass species and the reduced availability of Al, Cu, Fe, Pb and Zn in the TAGP treatments indicates that the overall reduction in dry matter yield at the higher liming rate was not caused by metal toxicity. Figures 7.11, 7.12 & 7.13 clearly indicate that both 0.1M HCl and 0.02M CaCl₂ extractable Cu, Fe, Pb and Zn concentrations at the TAGP liming are comparatively much lower than those of the other treatments. Similarly 1M KCl extractable Al levels are relatively very low at this liming rate (Figure 7.13). The negative yield response associated with the TAGP liming rate is instead considered to have resulted from induced nutrient deficiencies arising from the immobilisation of nutrients within the amended tailings and/or the loss of nutrients from the tailings.

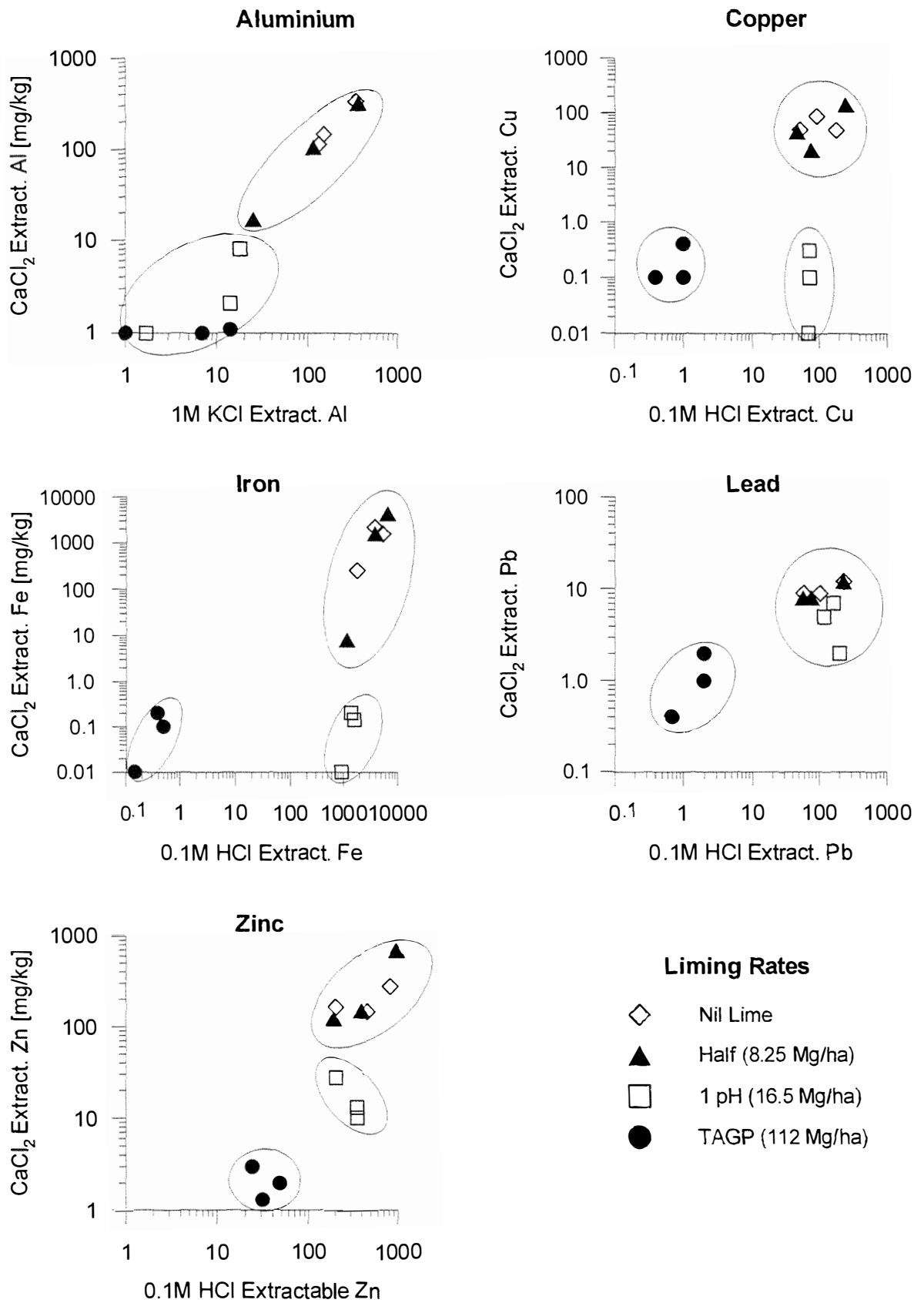


Figure 7.13 Relationships between 1M KCl and 0.02M CaCl₂ extractable Al, and between 0.1M HCl and 0.02M CaCl₂ extractable Cu, Fe, Pb and Zn [mg/kg]. The 3 data points for each treatment originate from analysis of unsown control pots conducted at week 3 (sowing), week 7 and week 11 (termination) of the trial.

As previously discussed, the addition of the equivalent of 112 Mg CaCO₃/ha was found to increase the pH of the tailings to about 7.5 where it remained relatively constant for the duration of the experiment. Potential problems affecting plant growth associated with high pH are well recognised and include; enzyme inactivation, induced B, Cu, Fe, Mg, Mn, Zn and P deficiencies, accelerated N loss through leaching and volatilisation and secondary growth problems particularly with legumes (Doubleday 1972; McLean & Dekker, 1976; Gemmell, 1977; Mengel & Kirkby, 1987; Pulford, 1991).

7.6.5.3 Plant Nutrition

To investigate whether the ‘heavy’ liming rates were adversely affecting plant nutrition, foliar analysis was conducted on selected herbage from the two effective lime treatments (Table 7.10). The nutrient values presented in the Table 7.10 represent either average nutrient concentrations from individual analysis conducted on two replicate pots or average values from composite samples (ie. combined herbage from all 4 replicate pots). Low dry matter yields meant that composite samples were required for *L.corniculatus* at both liming rates and for *A.capillaris* var. Egmont. and *F.rubra* var. Lobi at the 1 pH-6 and TAGP liming rates respectively. The quantities of dry matter produced by both *A.capillaris* cultivars at the TAGP liming rate were unfortunately too low for foliar analyses to be carried out.

Included in Table 7.10 are nutrient data for Ca, K, Mg, N and P and estimated total uptake values calculated as per equation 7.2. The nutrient status of the herbage was classified as *satisfactory*, *low* or *very low* by comparing the foliar nutrient content of the herbage grown on the amended tailings with ‘critical’ nutrient values for *Trifolium repens* and *Lolium perenne* grown in soil (McLaren & Cameron, 1996). Herbage was classified as having *satisfactory* nutrient status where herbage concentrations $\geq$ critical value, *low* nutrient status where herbage concentrations $<$ critical value and *very low* status where herbage concentrations $<$ 50% critical value. It is recognised that the critical values reported by McLaren & Cameron (1996) are based on field trials as opposed to glasshouse trials and that their use as anything but a rudimentary guide to indicate potential deficiencies in the herbage derived from the pot trials would be inappropriate.

$$\text{Uptake [mg/kg]} = \text{mean pot yield [g]} * \text{nutrient [\%]} * 10,000 \quad [7.2]$$

Table 7.10 Nutrient content and estimated total nutrient uptake by herbage from selected treatments.
sat. = satisfactory; v.low = very low; nd = values not determined due to insufficient dry matter product.

	<i>Agrostis capillaris</i>						<i>Festuca rubra</i>			
	Lotus		Parys Mtn.		Egmont		Merlin		Lobi	
Liming Rate	pH-6	TAGP	pH-6	TAGP	pH-6	TAGP	pH-6	TAGP	pH-6	TAGP
Phosphorus [%]	0.10	0.08	0.27	nd	0.27	nd	0.34	0.27	0.25	0.12
Critical P [%]	0.3	0.3	0.3	-	0.3	-	0.3	0.3	0.3	0.3
P Status	v.low	v.low	low	-	low	-	sat.	low	low	v.low
Uptake [mg/kg]	181	97	1491	-	164	-	3104	1259	787	168
Nitrogen [%]	3.71	6.67	4.53	nd	4.29	nd	4.39	4.54	4.61	4.91
Critical N [%]	4.4	4.4	4.0	-	4.0	-	4.0	4.0	4.0	4.0
N Status	low	sat.	sat.	-	sat.	-	sat.	sat.	sat.	sat.
Uptake [mg/kg]	6680	8001	24940	-	2577	-	39734	21551	14738	6877
Calcium [%]	0.78	1.65	0.41	nd	0.61	nd	0.39	0.64	0.73	1.07
Critical Ca [%]	0.3	0.3	0.2	-	0.2	-	0.2	0.2	0.2	0.2
Ca Status	sat.	sat.	sat.	-	sat.	-	sat.	sat.	sat.	sat.
Uptake [mg/kg]	1401	1984	2250	-	368	-	3548	3054	2323	1502
Magnesium [%]	0.20	0.45	0.12	nd	0.15	nd	0.11	0.21	0.16	0.25
Critical Mg [%]	0.13	0.13	0.15	-	0.15	-	0.15	0.15	0.15	0.15
Mg Status	sat.	sat.	low	-	sat.	-	low	sat.	sat.	sat.
Uptake [mg/kg]	355	544	660	-	89	-	1032	1017	525	354
Potassium [%]	1.40	1.06	4.07	nd	3.28	nd	3.06	2.28	2.22	1.18
Critical K [%]	1.7	1.7	1.7	-	1.7	-	1.7	1.7	1.7	1.7
K Status	low	low	sat.	-	sat.	-	sat.	sat.	sat.	low
Uptake [mg/kg]	2512	1271	22391	-	1967	-	27693	10849	7101	1648

(i) Phosphorus

The most severe nutrient deficiency observed in the herbage was that of P which was found to be deficient in 7 of the 8 treatments analysed. Analyses of the tailings sampled from the equivalent control pots confirmed that the total P and Olsen P content of the tailings were very low over the duration of the trial despite the addition of soluble P fertiliser (Table 7.9). The deficiency of P is considered by many researchers to be the main factor limiting plant colonisation of mining wastes closely followed by N deficiencies (Smith & Bradshaw, 1979; Bradshaw & Chadwick, 1980; Barnishel *et al.*, 1982).

Herbage of the metal-tolerant cultivar of *F.rubra* (Merlin) grown on the lower of the two liming rates was the only foliage found to contain what were considered to be satisfactory levels of P (Table 7.10). This observation is important in that it was this treatment that yielded the greatest levels of dry matter which strongly suggests that P nutrition was an important factor governing the growth of the plants on the various treatments.

P deficiency was most marked in herbage originating from tailings amended with the TAGP rate of lime (Table 7.10). *L.corniculatus* and *F.rubra* var. Lobi were particularly deficient in P at the higher of the two liming rates, presumably due to the effective immobilisation of P in the tailings. In the case of *L.corniculatus*, very low P concentrations were observed in herbage obtained from both lime treatments. The inability of *L.corniculatus* to take up greater quantities of P may have at least in part reflected their poorly developed root systems which were clearly incapable of fully exploiting the substrate's P reserve.

As previously discussed (Chapter 3; section 3.7.3.1) the uptake of P is highly pH dependent. Soil pH not only regulates the ratio of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ in the soil solution but also governs the adsorption of P and formation of phosphatic complexes. In heavily limed growth media or in calcareous soils, the formation of precipitates of low solubility phosphates, such as tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), becomes an important mechanism governing the availability of this macronutrient. Most plants grown on the tailings showed some symptoms of P deficiency which is characterised by overall stunting of the leaf and root system, dark green mature foliage and reddening or purpling of the stems, petioles and leaves resulting from the accumulation of anthocyanins (Mengel & Kirkby, 1987; Salisbury & Ross, 1992). The strongest visual evidence of P deficiency was manifest in the dark green foliage of the grasses and discolouration of stems.

In other studies the application of heavy rates of lime to pyritic mine wastes has been found to have variable impact on the P nutrition of pastoral plant species (Doubleday, 1972; Gemmell, 1981; Costigan *et al.*, 1982). One common finding of these studies was

that the performance of legumes was more adversely effected by the application of high rates of lime than the grass species investigated. In the study of Costigan *et al.* (1982), for example, the application of lime in excess of 5 Mg/ha was found to significantly reduce the growth of *Trifolium repens* by as much as 90%, where as in the case of *Lolium perenne* this amount of lime was the minimum required to attain satisfactory germination and growth. Costigan *et al.* (1982) proposed that the application of high rates of P fertiliser and the substitution of Mg limestone (dolomite) for calcitic limestone could improve the growth response of *L.perenne* and reduce the inhibitory effects of high rates of calcitic limestone on *T.repens*.

In contrast to Gemmell (1981) and Costigan *et al.* (1982), Doubleday (1972) found that that the growth of *Lolium perenne* was significantly reduced by the application of high rates of lime. Doubleday (1972) reported that the growth responses of *L.perenne* to phosphate application on some spoils were reduced by over 80% after liming to pH 7.8. Even moderate rates of lime addition (sufficient to attain a pH of 6.5) were found to significantly reduce dry matter yields. Doubleday (1972) attributed this inhibition to lime-induced Fe deficiency and possibly the immobilisation of P and nutrient imbalances. This finding is consistent with those of the present study which indicate that the performance of *A.capillaris* and *F.rubra* as well as *L.corniculatus* was governed to a large degree by P availability. Although the herbage did not show obvious symptoms of Fe deficiency (interveinal chlorosis and in severe cases total bleaching of young foliage) analysis of the growing medium clearly indicates that availability of Fe in the tailings treated with the two highest rates of lime was very low (Figure 7.13). Because the herbage was not analysed for Fe, however, it is impossible to speculate whether the performance of the plants were adversely effected by Fe deficiencies.

(ii) Nitrogen

In contrast to phosphate levels, herbage N levels appeared to be mostly adequate at both the 1 pH-6 and TAGP liming rates (Table 7.10). *L.corniculatus* grown on the lower of the two rates, however, was found to contain less than 3.8% N, a level considered to indicate deficiency. This analytical finding is consistent with the chlorotic yellow appearance of the *L.corniculatus* seedlings grown on this treatment and strongly suggests that the low yields and poor performance of this species were at least in part

related to the inability of Lotus to take up sufficient N under the circumneutral pH conditions induced by applying 16.5 Mg CaCO₃/ha. Conversely, the heavier rate of lime appeared to improve the N status of *L.corniculatus* (Table 7.10). This findings is somewhat surprising in that the foliage of Lotus plants grown on this treatment also showed signs of chlorosis consistent with N deficiency. It is postulated that lime induced molybdenum deficiencies may^{have} alternatively adversely affected *L.corniculatus* growth.

Analysis of the unplanted control pots indicated that total N concentrations in the tailings were extremely low in all treatments at the end of the growing period despite the addition of appreciable quantities of ammonium nitrate (Table 7.9). It is postulated that in the absence of plant uptake, N was being lost from the tailings as a result of leaching and/or ammonia volatilisation. Coarsely grained materials devoid of organic matter and high CEC clays, such as the Tui mine tailings, are susceptible to leaching of certain plant nutrients including nitrate (Johnson *et al.*, 1977; Bradshaw & Chadwick, 1980). In those pots receiving the equivalent of 112 Mg CaCO₃ per hectare, gaseous losses of N may have further depleted N in the tailings. Previous research indicates that the volatilisation of ammonia (NH₃) produced by the dissociation of ammonium carbonate (NH₄)₂CO₃ is enhanced at high pH and can lead to significant losses of N in calcareous soils or in heavily limed mine-wastes (Reeder & Sabey, 1987).

(iii) Calcium & Magnesium

Predictably, the Ca status of the various taxa grown on tailings amended with both rates of lime were adequate (Table 7.10). In the case of *L.corniculatus* the percentage of Ca in the herbage was found to more than double at the higher rate of lime and was present in concentrations far in excess of that considered necessary for optimum growth (1.65% cf. 0.3%). The trends observed in the herbage are consistent with the concentrations of exchangeable Ca in the control pots (Table 7.9).

The presence of high concentrations of Ca in the tailings appears to have had little impact on the uptake of Mg. Like K⁺ and NH₄⁺, excessive concentrations of Ca²⁺ in soils can adversely affect the uptake the Mg²⁺ due to ion competition. This phenomenon is most commonly associated with calcareous soils (Mengel & Kirkby, 1987), but has

been noted in several studies investigating the reclamation of heavily limed colliery spoils (Doubleday, 1972; Gemmell, 1981; Costigan *et al.*, 1982). Previous research indicates that the substitution of dolomite for calcitic limestone helps prevent Mg deficiencies by reducing the competitive uptake of Ca^{2+} (Costigan *et al.*, 1982).

The relatively high levels of Mg found in the TAGP control pot indicates that Mg may have been immobilised at high pH by free carbonate (Table 7.9). It is highly unlikely that significant quantities of Mg were introduced through liming because analytical grade limestone (CaCO_3) was used in this experiment.

(iv) Potassium

Although the K status of some plants was low, the results presented in Table 7.10 indicate that K levels were generally adequate or only marginally deficient in most treatments. In the case of *L.corniculatus*, however, the herbage was found to be deficient at both liming rates. The non-tolerant *F.rubra* cultivar also appeared to exhibit K deficiency at the highest liming rate (Table 7.10).

Like Mg, K uptake and retention in plant cells is competitively affected by other ions. High concentrations of H^+ , Ca^{2+} , Mg^{2+} and Na^+ are known to adversely effect the uptake of this essential plant nutrient (Mengel & Kirkby, 1987). Foliar analysis of the herbage indicates that high concentrations of Ca may have induced K deficiency in the plants grown on the amended tailings, particularly those grown on the TAGP lime treated tailings.

7.6.6 Conclusions of Trial One

- The failure of all plant taxa to germinate on the unamended Tui tailings, including two varieties of metal-tolerant grass, confirmed that the tailings are an extremely hostile growth medium even for plants adapted to adverse growing conditions.
- The addition of lime at a rate equivalent to 8.25 Mg/ha ($\frac{1}{2}$ pH-6) did not adequately ameliorate the tailings' adverse germination conditions. Although pH levels initially improved upon lime incorporation, this rate of lime was found to, in fact, increase the relative bioavailability of some metals as the tailings re-acidified. This finding has important implications for any future attempts to reclaim the Tui Mine site. It

indicates that the application of what, by agricultural standards would be considered to be a high rate of lime (8.25 Mg/ha) to the tailings, may actually exacerbate growing conditions and acid mine drainage.

- It is evident that low pH, high electrical conductivity and phytotoxic metal concentrations in the soil solution all contributed to germination failure on the nil and $\frac{1}{2}$ pH-6 lime treatments.
- The addition of lime at rates ≥ 16.5 Mg/ha facilitated germination and plant growth of all taxa by reducing the pH and bioavailability of metals in the tailings. Plant nutrition, however, was adversely effected by these relatively heavy rates of lime application, particularly at the TAGP liming rate (112 Mg/ha) as indicated by foliar analysis.
- It appears that induced P deficiency was the primary reason for reduced plant growth yields on the TAGP lime treatment and that *F.rubra* (var. Merlin) was better adapted to absorbing this nutrient at circumneutral pH levels induced by heavy rates of lime application.
- Both varieties of *A.capillaris* were found to be poorly suited to the moderately alkaline conditions induced by the TAGP liming rate (112 Mg/ha). Likewise *L.corniculatus* performed poorly in this treatment, as it did at the lower liming rate (16.5 Mg/ha).
- Rhizobial inoculation of *L.corniculatus* failed to significantly^{improve} the performance of this species at either liming rate and visual inspection indicated no evidence of root nodulation. The poor performance of Lotus was particularly disappointing in that it is recognised that the establishment of a legume on the Tui tailings is fundamentally important to the formation of self-sustaining vegetative cover.
- In the short term (ie. <24 weeks), the 1 pH-6 liming rate was identified as being the superior treatment in terms of its ability to maintain the pH of the tailings in a range conducive to plant growth. The ongoing potential of the tailings to reacidify, however, was recognised as a major limitation to the long-term survival of plants established on this treatment. Contrary to what was predicted, reacidification of this treatment did not occur during the growth period, nor in the ensuing 3 months that the control pots were monitored.
- Whilst the growth of *F.rubra* var. Merlin was not considered to be optimal this taxa formed and maintained what was considered to be a 'satisfactory' vegetative cover on

tailings treated with 16.5 Mg CaCO_3 /ha throughout the 2 month growing period. Foliar analysis of the Merlin herbage grown on this treatment indicated that, with the possible exception of Mg, Merlin plants were receiving adequate macronutrients via the application of growth solution (Figure 7.10)

- Merlin was without doubt the most successful of the plant taxa trialed in terms of biomass produced and vigour. Whilst Merlin significantly out-yielded the non-metal-tolerant variety of *F.rubra* (var. Lobi) at both effective liming rates, a significant difference in yield between the metal-tolerant and non-metal tolerant *A.capillaris* cultivars was only noted at the lowest effective liming rate (1 pH-6 rate). Both cultivars of *A.capillaris* performed very poorly upon the TAGP lime treatments (Figure 7.8).
- Whilst literature pertaining to the reclamation of pyritic mines wastes commonly advocates the use of very high rates of lime to facilitate the growth of vegetation and to lessen the likelihood of acid mine drainage, the results of this trial suggest that there is a trade-off between diminished plant response resulting from the application of high rates of lime and the need to ensure sufficient lime is added to prevent reacidification of the growing medium and the generation of AMD. Although the addition of lime at the TAGP rate is likely to have effectively prevented reacidification of the tailings, the adverse nutritional effects associated with this liming rate are unlikely to facilitate the establishment of an effective vegetative cover.

7.7 Trial Two - Organic Matter Amendment

7.7.1 Aim

The primary aim of this trial was to investigate the effect of the addition of an organic matter amendment on the plant growth characteristics of the Tui mine tailings. Various rates of composted sewage sludge were evaluated, both with and without the addition of lime, to assess the impact of these treatments on the growth performance of two plant species, *Lotus corniculatus* and *Festuca rubra* var. Merlin. The liming rate was decreased with increasing rates of sludge addition to account for the neutralising effect of the sludge.

7.7.2 Trial Design

The growth responses of *L.corniculatus* (Lotus) and *F.rubra* (Merlin) were monitored over an 8 week period on tailings amended with four rates of composted sewage sludge and two rates of lime. A completely randomised block design trial comprised of 4 sludge rates, 2 liming rates and 2 plant species with four replicates was used (Table 7.11). An additional 8 amended but unsown control pots were included in the trial, thus a total of 72 pots were used in Trial Two (Plates 7.5 & 7.6). The control pots were destructively sampled and analysed during the course of the trial to monitor the growth conditions of the tailings(section 7.5).

Table 7.11 Trial Two design and amendment rates. Liming rates: nil = nil lime treatment, 1 pH 6 = amount of lime required to raise the pH of the sludge amended tailings to approximately 6.0.
Fr = *Festuca rubra* (var. Merlin), Lc = *Lotus corniculatus*

Sludge Rate [Mg/ha]	0	110	220	440
g/kg tailings	0	78	156	312
Liming Rates	nil, 1 pH 6	nil, 1 pH 6	nil, 1 pH 6	nil, 1 pH 6
Plant Species	Fr, Lc	Fr, Lc	Fr, Lc	Fr, Lc
Treatment replicates	4	4	4	4

The characteristics of the two plant taxa used in the glasshouse trial are outlined in Table 7.4. It was deemed important to include a legume such as Lotus in this trial because as discussed in Chapter 3 (section 3.7) legumes aid in the development of a

self-sustaining soil-plant ecosystem by reducing or eliminating the need for supplementary nitrogen application.

7.7.3 Trial Methodology

7.7.3.1 Sludge Addition

The North Shore sludge⁷ used in this trial was incorporated into the tailings at 4 different rates; 0, 110, 220 and 440 Mg/ha. The highest rate (440 Mg/ha) was based on the amount of sludge required to elevate the organic carbon content of the tailings to approximately 4 % (Appendix 7(B)). This level is comparable to many of New Zealand's soils which typically contain between about 4 and 10% organic carbon (Blakemore *et al.*, 1987) and is in excess of the minimal amount that Johnson *et al.* (1994) suggest should be incorporated into mining wastes (1.8%). As discussed in Chapter 3 (section 3.7.4) sludge application rates in excess 400 Mg/ha are commonly used in the reclamation of mine wastes. In some overseas trials outlined by Sopper (1992) application rates in excess of 900 Mg/ha have been evaluated.

The sludge rates used in this trial were calculated based upon a 200 mm incorporation depth and used organic carbon analysis of the sludge (Table 7.2) conducted by Limpus-O'Reilly (1997). Prior to amendment addition, samples of the sludge were oven-dried at 105 °C for 24 hours to assess its water content. The sludge was found to contain about 46 % water by mass, therefore the highest sludge rate treatments (440 Mg/ha) required the addition of approximately 312 g of moist sludge to each kilogram of oven-dry tailings (Table 7.11). To ensure thorough mixing of the plant growth media the various sludge treatments were weighed out individually and then added to numbered plastic bags containing one kilogram of oven-dry tailings and one of two rates of lime; either a nil rate, or a rate calculated to raise the pH of the sludge amended tailings to 6.0 (Table 7.12).

⁷ See description of sludge in section 7.1.3



Plate 7.5 Trial Two: 4 weeks after sowing.

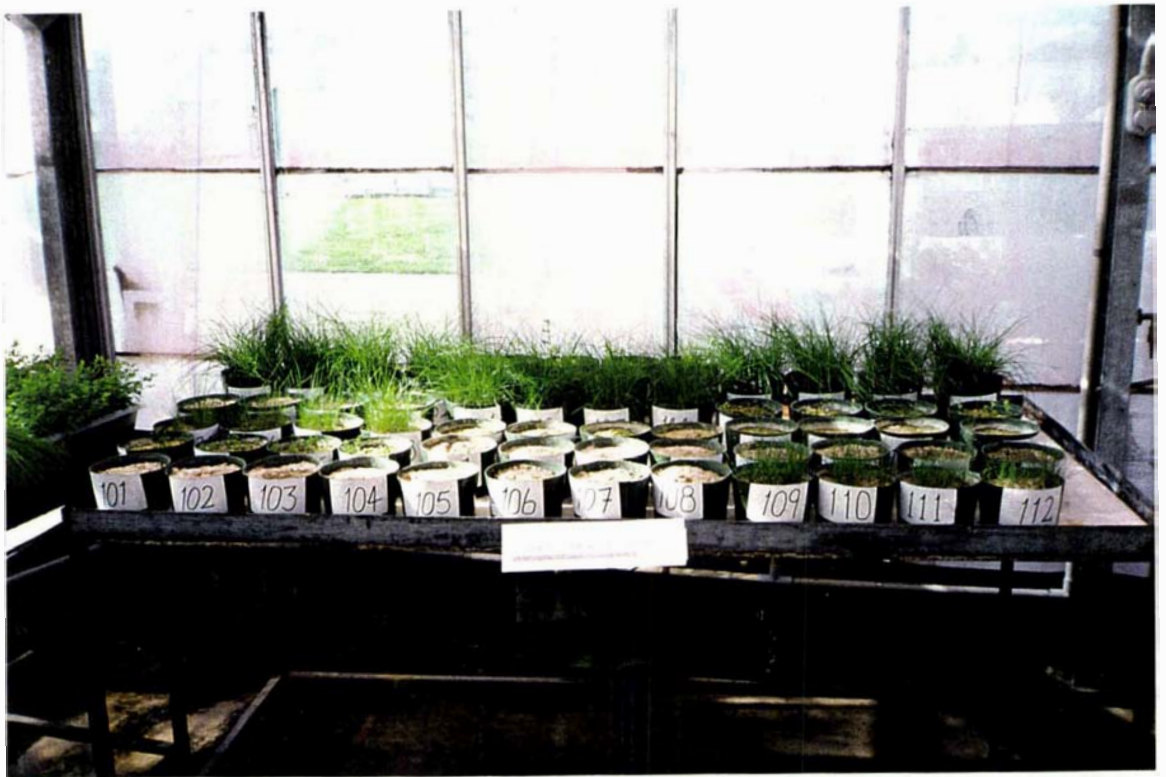


Plate 7.6 Trial Two: 8 weeks after sowing immediately prior to the herbage harvest.

7.7.3.2 Liming Requirements & Lime Addition

To ensure that the liming requirements of the amended tailings were accurately met and that the lime rapidly reacted with the tailings, finely ground (<150) analytical grade CaCO₃ was again used in this trial.

Due to the liming effect of the sludge, the amount of lime required to achieve pH 6 (1 pH-6 rate) as determined by a short-term pH buffering experiment (section 7.1.1.1), varied in relation to the rate of sludge added. Figure 7.1b clearly indicates that as the sludge rate was increased less lime was required to raise the pH of the tailings to 6.0. The different liming requirements of the various sludge amended treatments are presented in Table 7.12. As previously mentioned, the four rates of sludge outlined in Table 7.12 were evaluated both with and without lime addition, thus a total of 8 amendment treatments were assessed in Trial Two.

Table 7.12 Lime and sludge application rates for Trial Two treatments. The area rate assumes amendment incorporation to 200 mm depth and a tailings’ bulk density of 1.3 Mg/m³.

Sludge/Lime Levels	1 pH-6 Liming Rate			
Sludge Application Rate [Mg/ha]	nil	110	220	440
Lime [Mg/ha]	16.5	10.1	8.5	5.1
Lime [Mg/1000 Mg tailings]	6.33	3.88	3.25	1.97

7.7.3.3 Sowing

Each of the trial pots was sown with a rate of seed designed to apply approximately 100 viable seeds of the appropriate taxa (section 7.4). To help optimise the growth of Lotus all pots sown with this species were treated with an appropriate commercial Rhizobial inoculum.

7.7.4 Hypotheses

Dry matter yields for both plant species were expected to increase with increasing sludge application rates as the physical and chemical growing conditions in the tailings improved (Chapter 3; section 3.7.4). Sludge addition not only increases the organic matter content of the tailings but also acts as a liming agent and therefore reduces the

liming requirement of the tailings. The metal tolerant grass cultivar Merlin was predicted to substantially out-yield Lotus on the non-limed treatments due to Merlin's presumed lower Ca nutritional requirements and the supposed ability of this grass cultivar to tolerate Cu and to a lesser degree Pb and Zn contaminated substrates (Chapter 3; section 3.7.5).

The addition of lime to the sludge treated tailings at rates sufficient to increase the pH of the amended tailings to 6.0 was predicted to substantially improve plant performance and to reduce dry matter yield differences between Lotus and Merlin. The legume was predicted to perform better in the limed treatments due to the greater calcium concentrations and the immobilisation of potentially toxic heavy metals under the more neutral pH conditions.

7.7.5 Germination Results

7.7.5.1 Germination Trends on Non-Limed Treatments

Predictably and in keeping with the results of Trial One, both Lotus and Merlin failed to germinate on the untreated tailings (ie. nil sludge and nil lime treatment). The addition of 110 Mg/ha sludge only marginally improved germinating conditions in the tailings (Figure 7.14a). The few seedlings that emerged on this treatment were found to die back within 4 weeks of sowing. The addition of sludge at rates of ≥ 220 Mg/ha, however, was found to substantially improve germination conditions and seedling establishment conditions in the short-term at least. Germination rates in the vicinity of 40% were attained for both Lotus and Merlin at the 220 Mg sludge rate, however, the rate of seedling mortality was high, particularly for Lotus. By week four of the trial all of the Lotus seedlings had died and little more than half of the Merlin seedlings remained (Figure 7.14a). The surviving Merlin plants were generally unhealthy and relatively small and many of the tillers exhibited brown and purple hues. These symptoms are characteristic of phosphorus (P) deficiency and various metal toxicities. Regression (ie. die-back) of the Merlin plants continued to occur through the growing term.

At the 440 Mg/ha sludge rate, Lotus exhibited similar germination trends to those observed at the 220 Mg/ha sludge rate and despite the high rate of sludge addition most of the seedlings died-back within two weeks of sowing (Figure 7.14a). Regression of the

Lotus seedlings continued through the growing period to the extent that at harvesting only one of the four treatment pots yielded sufficient dry matter (0.01g) to warrant measurement. In contrast, Merlin germinated and fared well on the 440 Mg/ha treatment. A germination rate of about 60% was attained and seedlings grew vigorously throughout the trial. The plants showed no obvious signs of regression or nutrient imbalances.

7.7.5.2 Germination Trends on Limed Treatments

The overall effect of lime addition was to improve seed germination and seedling survival rates. The impact of liming was most noticeable on treatments that received nil, 110, or 220 Mg/ha rates of sludge (Figure 7.14b). The addition of lime to the non-sludge treated tailings enabled Lotus and Merlin to germinate moderately well (Figure 7.14b). Whilst relatively high average germination rates in the vicinity of 60% were attained for both species and seedling survival rates were high, dry matter yields from this treatment were poor (Figure 7.14b). These results corroborate those of Trial One in which the nil sludge and 1 pH-6 lime treatment was effectively duplicated (Figures 7.4b & 7.5).

The germination and seedling survival rates of Merlin showed little variability amongst those treatments that received both lime and sludge. Germination rates for this taxa were in the vicinity of 50 to 60 % in each of the 3 sludge amended treatments and seedling mortality was low during the 4 week monitoring period (Figure 7.14b). The germination results indicate that the variations in Merlin dry matter production between the limed treatments was primarily a function of plant size rather than seedling numbers. The average germination rate of Merlin on the 440 Mg/ha treatment, for example, was comparatively low but significantly out yielded the other treatments (Figures 7.14b & 7.15b).

In terms of germination, Lotus showed a greater degree of variability between the various limed treatments than Merlin (Figure 7.14b). Within one week of sowing the average germination rate attained from those pots treated with 110 Mg/ha sludge and the equivalent of 10.1 Mg/ha of lime was approximately $67 \pm 9\%$ (this compares with a germination rate of just $7 \pm 3\%$ on the equivalent non-limed treatment, Figure 7.14a). Despite the addition of this relatively high rate of lime and sludge by week 4 of the trial

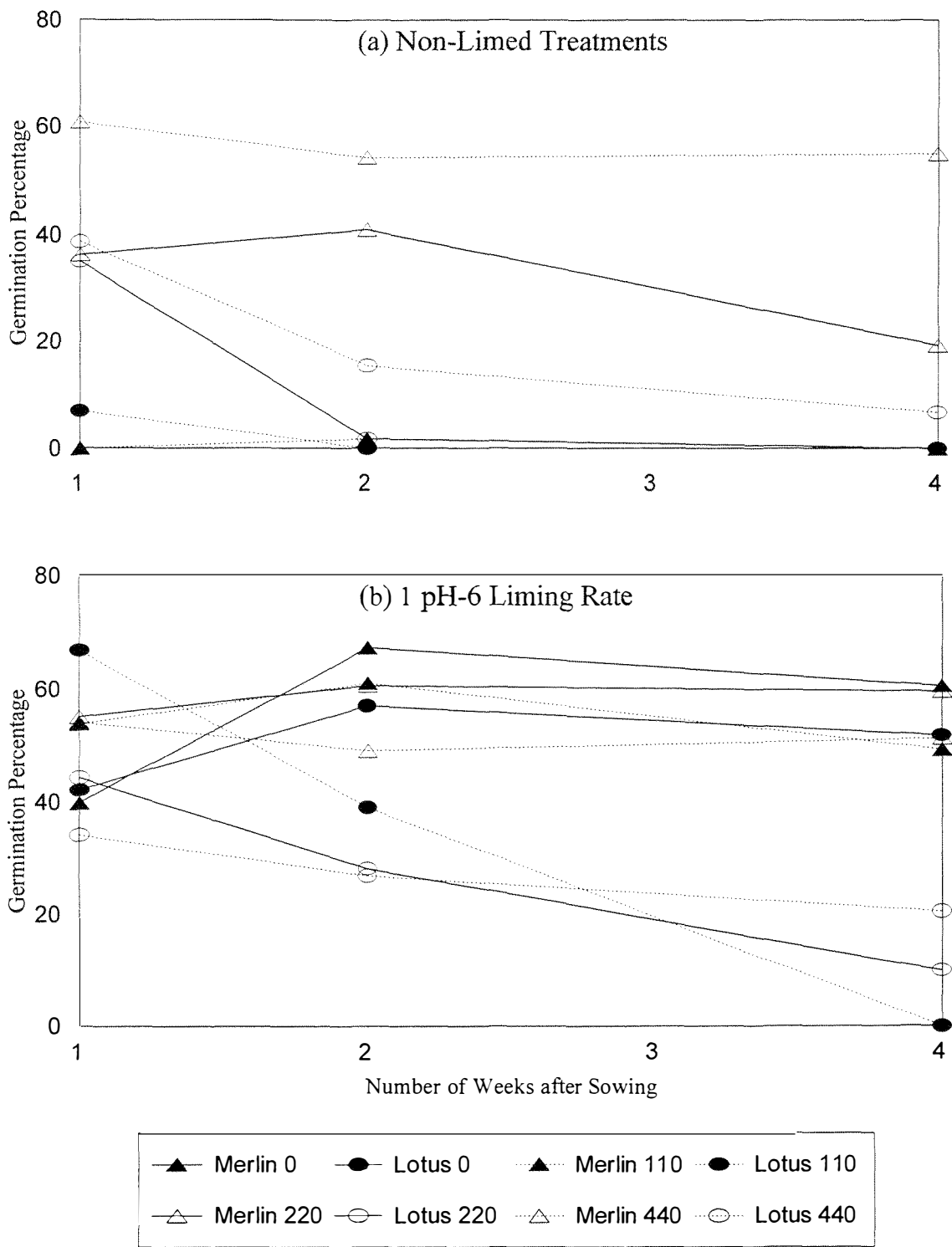


Figure 7.14 Percentage germination at various periods after sowing in (a) non-limed, sludge amended tailings and (b) sludge amended tailing limed to pH 6.0.

all of the seedlings had died. Similar germination and seedling survival trends were exhibited by Lotus sown on the limed 220 and 440 Mg/ha sludge treatments. The initial germination rates for these two treatments were in the vicinity of 40%. The majority of the seedlings, however, died prior to the end the growing period (Figure 7.14a & 7.14b).

At the 440 Mg/ha sludge rate the addition lime at a rate equivalent to 5.1 Mg/ha had little effect on the germination of Merlin and Lotus (ie. germination and seedling survival trends were comparable to those at the 440 Mg/ha sludge treatments that received no lime). Although Merlin seedlings established well on the limed 440 Mg/ha sludge treatment and grew vigorously throughout the experiment, the majority of the Lotus seedlings that germinated died-back during the germination monitoring period and in the ensuing weeks.

7.7.6 Dry Matter Yields

7.7.6.1 Non-Limed Treatments

Without lime addition the performance of Lotus on the various sludge treatments was extremely poor (Figure 7.15a). No significant quantities of dry matter were produced from any of the non-limed pots sown with Lotus. The only pot to successfully yield any dry matter was one of four pots that had been amended with sludge at rate equivalent to 440 Mg/ha. The quantity of dry matter produced from this pot (0.01 g) originated from a few seedlings that were clearly unhealthy and regressing.

In the case of Merlin, analysis of variance (ANOVA) indicated that significant yields of this taxa were only attained from those pots treated with 440 Mg/ha sludge (Figure 7.15a). Although small yields of Merlin were also produced from each of the four pots treated with 220 Mg/ha sludge, they were not significant. In the absence of lime these pots produced an average of just 0.032 ± 0.005 grams/pot of dry matter. As previously discussed (section 7.7.5.1) the seedlings established on this treatment were unhealthy and exhibited symptoms of P deficiency characterised by dark green foliage and numerous brown and purple tillers. The identification of high Olsen P levels in the treatment control pot (ie. in the absence of plants), however, casts doubt as to whether the plants were indeed P deficient or whether Olsen P is suitable for assessing P availability in sludges (Table 7.13).

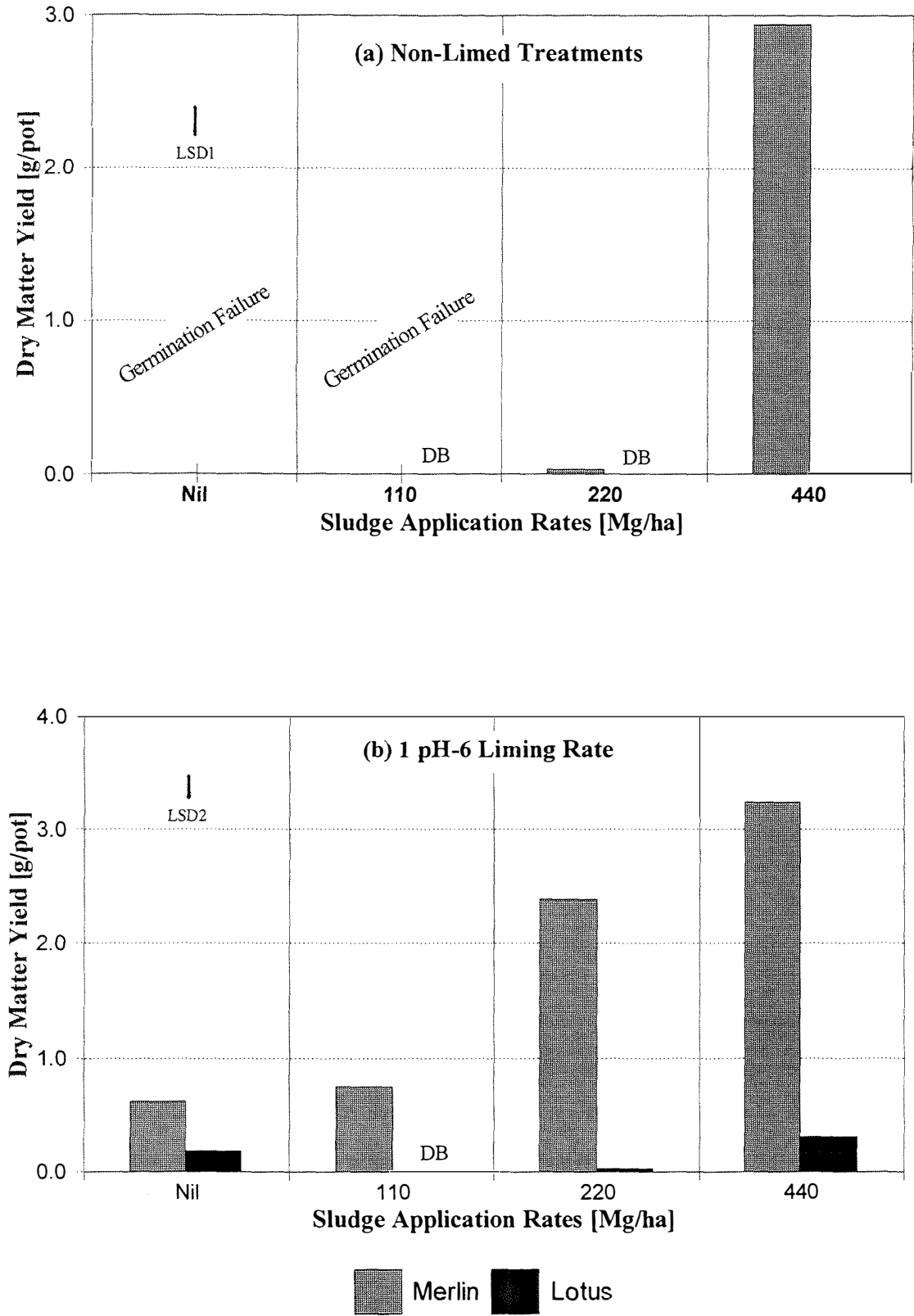


Figure 7.15 Dry matter yields of *Festuca rubra* (Merlin) and *Lotus corniculatus* in (a) non-limed tailings and (b) tailings limed initially to pH 6.0. DB = indicates that total Die Back of seedlings occurred. LSD1 = Least significant difference (species/rate interaction) on non-limed treatments (5%); LSD2 = Least significant difference (species/rate interaction) on 1 pH-6 treatments (5%).

Doubling the rate of sludge application from 220 Mg/ha to 440 Mg/ha increased dry matter yields of Merlin dramatically (Figure 7.15a). At the higher sludge rate a 90-fold increase in yield was noted with each pot producing an average of 2.94 ± 0.39 grams of dry matter. ANOVA confirmed that the sludge had a very highly significant ($P < 0.001$) positive effect on dry matter yield and that the interaction between sludge and plants species was very highly significant. Plate 7.7 shows the comparative growth of Merlin 4 weeks after sowing on various treatments. It is evident that 'satisfactory' growth was attained at the highest sludge treatment only (pot 152).



Plate 7.7 This photograph taken 4 weeks after sowing compares the growth of *F. rubra* (Merlin) grown on tailings amended with 4 different rates of sludge; nil, 110, 220 and 440 Mg/ha. Sludge rate increases from left to right.

(i) pH

In the absence of lime, growth failure on the nil and 110 Mg/ha sludge treatments is clearly attributable to the extremely low pH of the tailings throughout the germination and growing period (Figure 7.16a). The pH of the nil-treatment control remained in the vicinity of 2.1 for the duration of the trial, a pH level consistent with that of the nil-treatment control in Trial One (Figure 7.5). Although the addition of 110 Mg/ha of

sludge to the tailings initially elevated the pH of the tailings to about 3.3, the pH of this treatment dropped rapidly during the trial to the point where by at week 11 (termination) there was no difference between the pH of untreated tailings and 110 Mg/ha sludge treated tailings (Figure 7.16a). Analysis of the ^{tailings}from the sown trial pots conducted at the end of the growing period (week 11) confirmed that the average pH of the nil sludge treatment was practically identical to that of 110 Mg/ha sludge treatment (Table 7.14). These values were comparable to but slightly higher than the pH values of the two control pots (Figure 7.16a).

The application of sludge at a rate equivalent to 220 Mg/ha was found to elevate the pH of the tailings to about 4.0, where it was maintained for 9 weeks before gradually decreasing. By the end of the growing period (week 11) the pH of the sown pots had fallen to 3.78 ± 0.35 . The pH of the 220 Mg/ha sludge rate control pot continued to drop in the ensuing weeks and by week 24 of the trial the amended tailings exhibited a pH of less than 2.8 (Figure 7.16a). As previously discussed, both species germinated moderately well on this treatment despite the acidic conditions. Regression of the plants during the growing period, however, resulted in the failure of Lotus to produce any significant dry matter and substantially reduced the quantities of herbage produced by Merlin (Figure 7.15 a). The die-back of established seedlings that occurred towards the latter stages of the trial appears to be either directly related to acidification of the tailings or alternatively to pH induced metal toxicity.

The addition of sludge at a rate equivalent to 440 Mg/ha effectively raised the pH of the tailings to between 4.5 and 4.9 for duration of the 8 week growing term and unlike the other treatments no marked decrease in pH was noted post sludge addition (Figures 7.16a). The large difference in yield between the 220 and 440 Mg/ha sludge treatment suggests that a critical pH value exists between pH 3.80 and 4.7 below which the performance of Merlin is significantly impaired presumably due to the increased activity of hydrogen ions and phytotoxic metals.

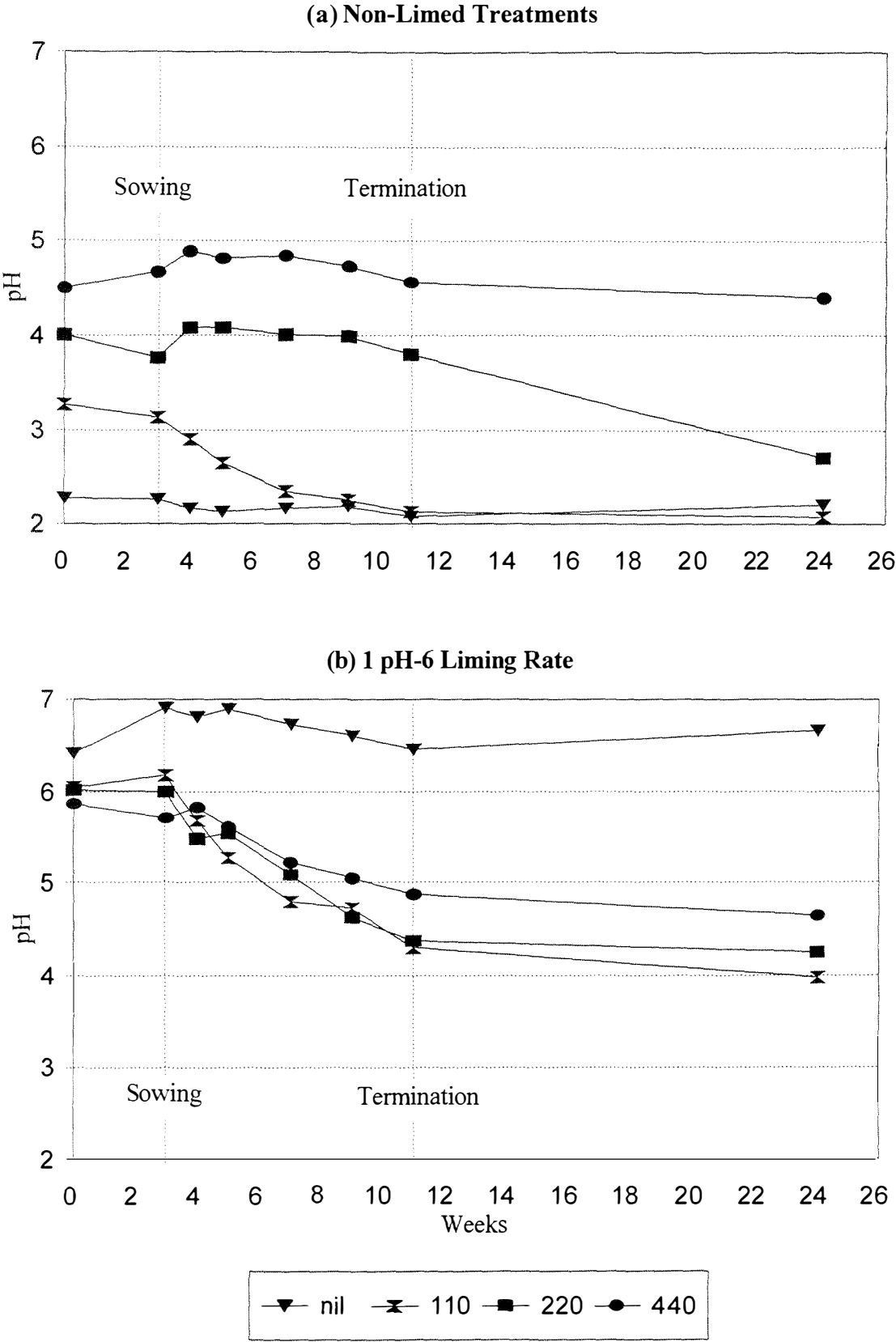


Figure 7.16 Changing pH of sludge treated tailings (control pots) (a) without lime addition and (b) initially limed to pH 6.0. Sludge rate units in legend = Mg/ha.

(ii) Extractable Metals

To elucidate the role of metal phytotoxicity in this trial the ‘plant available’ metal concentrations were measured using 0.02M CaCl₂ and 0.1M HCl on three occasions during the course of the trial (section 7.5). One of the overall trends identified from these analyses was that the addition of sludge to the tailings generally served to decrease the concentrations of 0.02M CaCl₂ extractable metals in the tailings (Figures 7.17-7.18). Comparison of 0.02M CaCl₂ extractable metal concentrations in the nil and 110 Mg/ha sludge treatments with the critical soil solution levels presented in Table 7.1 clearly indicates that some elements including Al, As, Cd, Cu, Fe and Zn were present in concentrations likely to be phytotoxic. The particularly high concentrations of Al, Cu and Fe in both the nil and 110 Mg/ha sludge treatments readily explain the failure of Merlin and Lotus to successfully germinate and establish on these treatments (Figures 7.17 & 7.18). The problems contributing to germination failure at low pH have been discussed in Trial One (section 7.6.5.2).

At the two higher sludge rates (220 and 440 Mg/ha) 0.02M CaCl₂ extractable metal concentrations were comparatively much lower (Figures 7.19 & 7.20). Although none of the elements determined appeared to be present at phytotoxic concentrations in the 440 Mg/ha sludge treatment, what are believed to be potentially phytotoxic concentrations of Al (18 mg/kg), Cu (11 mg/kg) and Zn (661 mg/kg) were identified in the 220 Mg/ha sludge treatment mid-way during the growth period (Figure 7.19). The presumably greater bioavailability of these metals at the 220 Mg/ha rate explains the failure of this treatment to yield significant quantities of herbage and may explain discolouration of the herbage.

It is important to note that sludge addition did not necessarily result in the net reduction of metal availability in sludge treated tailings. The concentrations of Al, Cd, Cu and Zn in the 110 Mg/ha sludge treatment, for example, were at week 7 and week 11 higher than those in the treatment that received no sludge (Figure 7.21). Similarly, 1M KCl extractable Al and 0.1M HCl extractable Cd and Cu were also found in greater concentrations in the 110 Mg/ha sludge treatment (Figure 7.22). This finding is significant in that it indicates that sulphide oxidation and the associated release of metal sulphates may have been enhanced by the addition of this relatively low rate of sludge.

The 110 Mg/ha sludge treated tailings were also found to exhibit higher electrical conductivity (Figure 7.2a) and phosphate extractable sulphate levels (Figure 7.3b) which further substantiates this hypothesis. The apparent ‘catalytic’ effect afforded by this low rate of sludge parallels research findings in Trial One which similarly found that a low rate of lime addition appeared to exacerbate metal availability (section 7.6.5.2). Clearly this finding once again has important implications for future attempts to reclaim the site should it involve amendment with organic waste and warrants further investigation.

The very low concentrations of *readily available* (0.02M CaCl₂ extractable) metals in the 220 and 440 Mg/ha sludge treatments are considered to result from simple pH induced precipitation of metal compounds, specific adsorption (including chelation) and cation exchange. Figure 7.16a demonstrates that the addition of sludge at rates ≥ 220 Mg/ha substantially increased the pH of these two treatments. In addition to reducing the solubility of metals, the more alkaline conditions are also likely to have at least partially inhibited biochemical oxidation of remnant sulphide minerals within the amended tailings and hence reduced the liberation of metal sulphates into solution.

Predictably, the levels of metals extracted with 0.1M HCl were generally significantly higher than those extracted with 0.02M CaCl₂ (Figures 7.17-7.20). Whereas *readily available* (0.02M CaCl₂ extractable) metal concentrations were generally reduced by increasing the sludge application rate, 0.1M HCl levels tended to be less effected by sludge addition and in the cases of Mn, Pb and Zn the application of sludge actually served to increase the extractable concentrations of these metals in the tailings to varying degrees (Figures 7.17 - 7.20). In contrast, and in keeping with 0.02M CaCl₂ extraction trends, concentrations of 0.1M HCl extractable Al and Fe decreased substantially with the addition of sludge (Figure 7.22). The changes in metal availability (0.1M HCl extractable) in response to sludge addition are most readily observed in Figure 7.22.

A variety of mechanisms, including simple dilution and contamination (associated with sludge addition), precipitation, chelation and cation ion exchange were undoubtedly responsible for governing the availability of individual metals within the various treatments. Although some trends observed in the metal analysis data were not readily explained by the relative concentrations of metals in the sludge or tailings, it is clear that

in terms of metal availability, sludge addition was beneficial in treatments where it was applied at rates equal to or in excess of 220 Mg/ha. Furthermore, it appears that Al, Cu and Zn were only effectively reduced below phytotoxic levels in the 440 Mg/ha sludge treatment.

(iii) Nutrients

As previously discussed, the addition of sewage sludge to mining wastes can serve to improve the fertility status of such materials by providing a variety of plant nutrients (Chapter 3; section 3.7.4.1). Soil chemical analysis of the various treatments amended with composted sewage sludge indicates that the addition of sludge was indeed beneficial in terms of improving the fertility of the Tui tailings (Table 7.13). The most obvious effect of sludge addition was the augmentation of the tailing's nitrogen (N) and phosphorus (P) reserves (Table 7.13).

Total N levels were increased from extremely low concentrations in the non-sludge amended tailings to much greater levels, particularly in the 440 Mg/ha sludge treatments. Similarly, total P levels in the tailings were increased from very low concentrations in the unamended tailings to average concentrations in the 110 Mg treatment and to what Blakemore *et al.* (1987) classify as very high concentrations in both the 220 and 440 Mg/ha sludge treatments (Table 7.13).

The levels of Olsen-soluble P were also found to dramatically increase with sludge addition due to its high inherent P content (Table 7.13). Upon sowing very high Olsen P values of 79 and 92 mg/kg were determined in the 220 and 440 Mg/ha sludge treatments respectively. In contrast, Olsen P levels in the unamended tailings were about 3.5 mg/kg (Table 7.13). Levels of exchangeable calcium were also found to increase with increasing sludge addition. High exchange Ca levels were identified in tailings amended with rates of sludge ≥ 220 Mg/ha (Table 7.13). Exchangeable potassium and sodium levels in contrast were not found to increase noticeably with sludge addition. Sludge addition similarly appeared to have little effect on the overall cation exchange capacity (CEC) of the tailings. The 'effective' CEC of the tailings is, however, postulated to have improved as the proportion of exchange sites associated with organic matter increased. Sludge addition was also found to improve the tailings' Mg status (Table 7.13).

Whilst in theory the application of a complete nutrient growth solution to all pots should have eliminated the nutritional effects of sludge, nutrients derived from the sludge (particularly N and P) may have at least partially contributed to dry matter production trends observed in this experiment. Clearly the availability of N and P in the 440 Mg/ha sludge treatment was much higher than that in the 220, 110 and nil sludge treatments. Of these two nutrients N is likely to have been more limiting than P which was present in relatively high concentration in all bar the nil-sludge treatment (Table 7.13).

Table 7.13 Soil fertility parameters of Trial Two non-limed control pots determined at sowing (Week 3) and at the end of the growing period (Week 11). Medium values for New Zealand soils are based on the data of Blakemore *et al.* (1987). *Values are expressed as mg/kg. [†] Values expressed as meq/100g .
nd = not determined

Soil Parameter	Medium Values	Sludge Application Levels [Mg/ha]							
		nil		110		220		440	
		Week 3	Week 11	Week 3	Week 11	Week 3	Week 11	Week 3	Week 11
pH	5.3-6.5	2.27	2.08	3.14	2.13	3.77	3.80	4.67	4.56
Olsen P*	20-30	3.5	0.1	44	24	79	85	92	110
Total P*	400-800	nd	58.2	nd	575	nd	1369	nd	2047
Total N*	3000-6000	nd	13.0	nd	620	nd	1484	nd	2869
Sulphate*	15-50	1245	4008	1275	1503	1365	1809	1410	1859
Exch. Ca [†]	5.0-10.0	0.6	0.6	7.1	5.7	10.8	11.4	14.0	14.8
Exch. K [†]	0.5-0.8	0.01	0.08	0.08	0.11	0.05	0.15	0.08	0.18
Exch. Na [†]	0.3-0.7	0.1	0.1	0.1	0.3	0.3	0.3	0.2	0.2
Exch. Mg [†]	1.0-3.0	0.10	0.09	0.45	0.40	0.64	0.54	0.87	0.72
CEC [†]	12-25	15	29	18	32	20	22	24	23

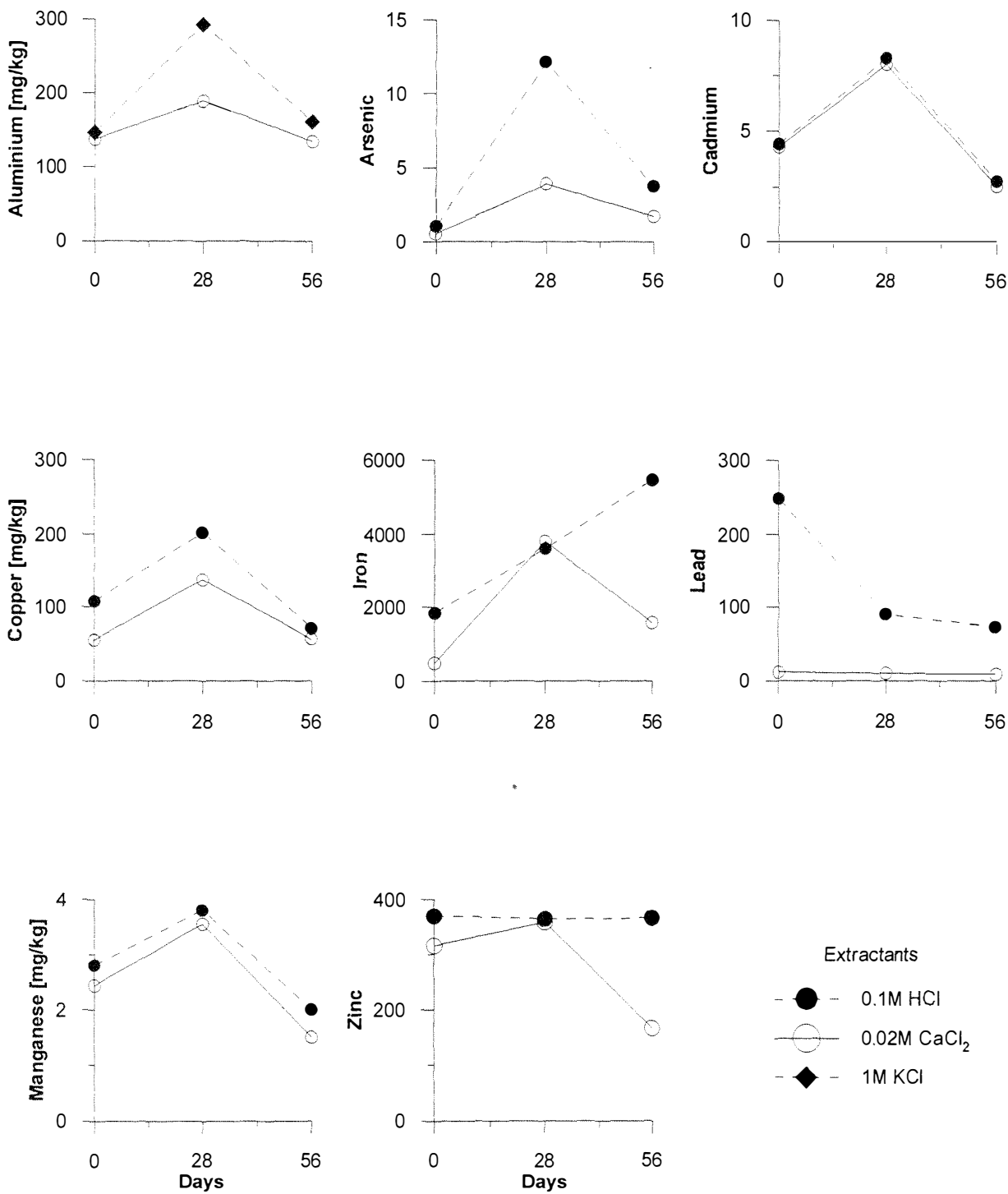


Figure 7.17 Changes in metal concentrations as extracted by 0.1M HCl (●), 0.02M CaCl₂ (○) and 1M KCl (◆) for nil treated tailings during the growth period.

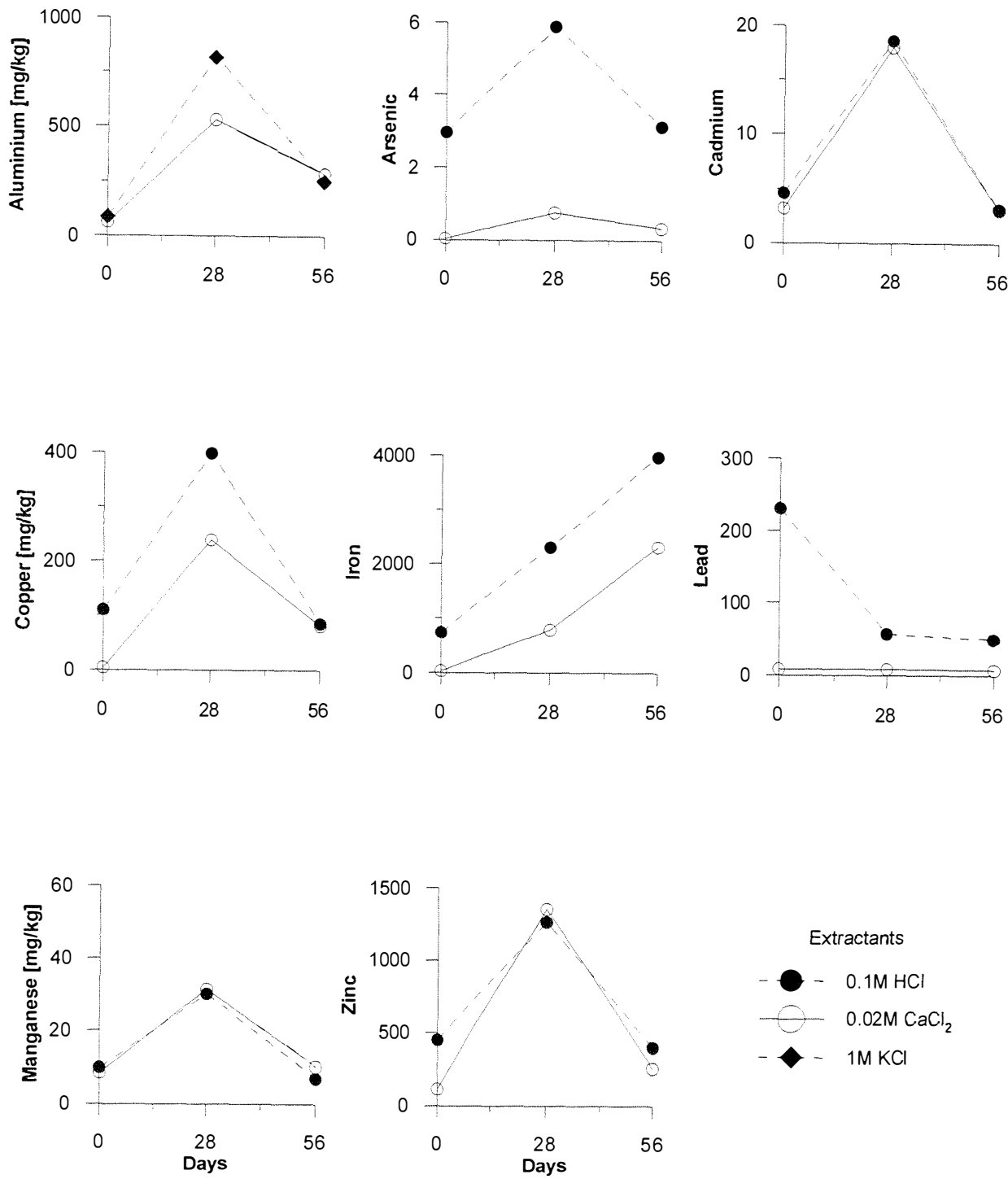


Figure 7.18 Changes in metal concentrations as extracted by 0.1M HCl (●), 0.02M CaCl₂ (o) and 1M KCl (◆) for 110 Mg/ha sludge treated tailings during the growth period.

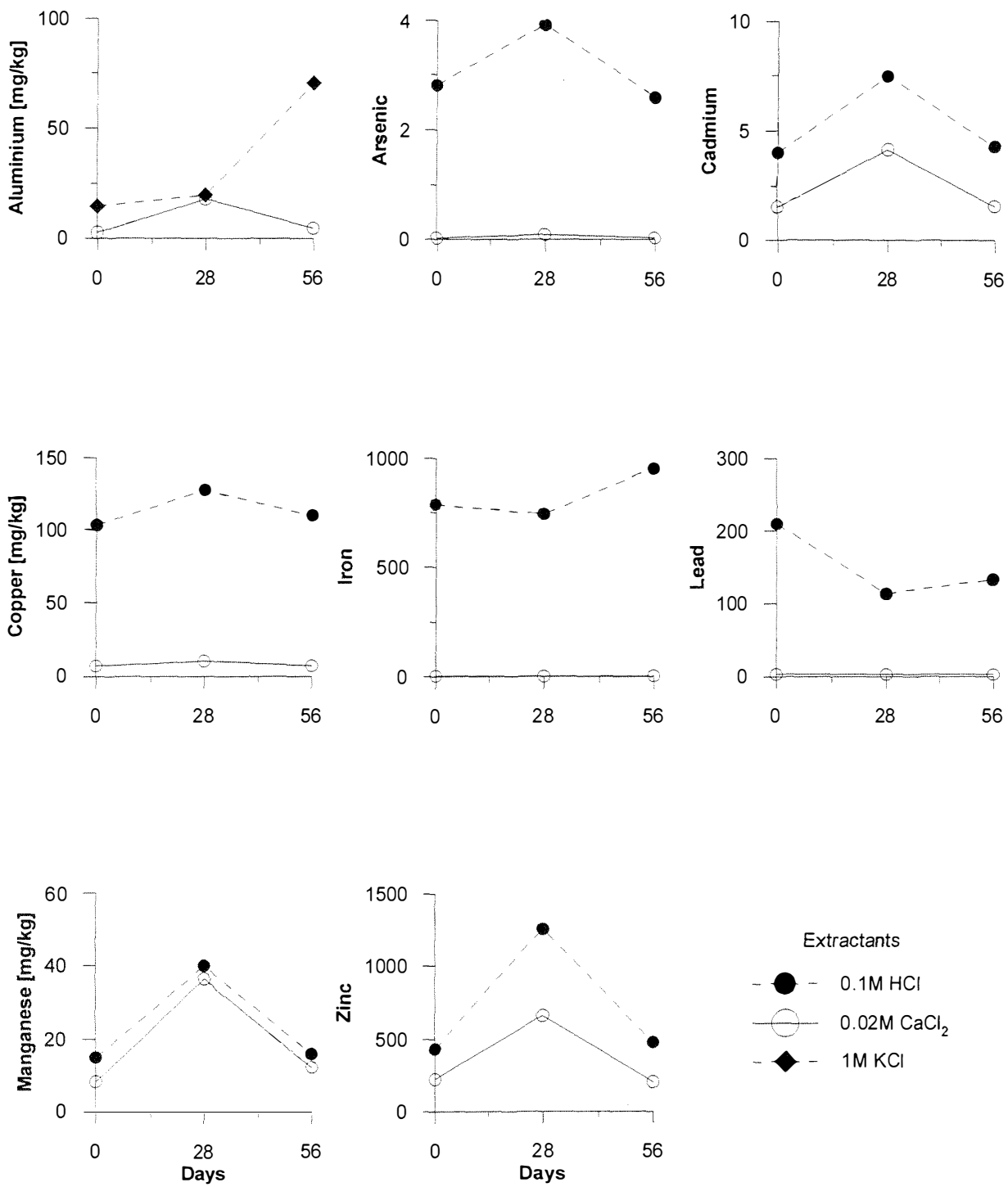


Figure 7.19 Changes in metal concentrations as extracted by 0.1M HCl (●), 0.02M CaCl₂ (o) and 1M KCl (◆) for 220 Mg/ha sludge treated tailings during the growth period.

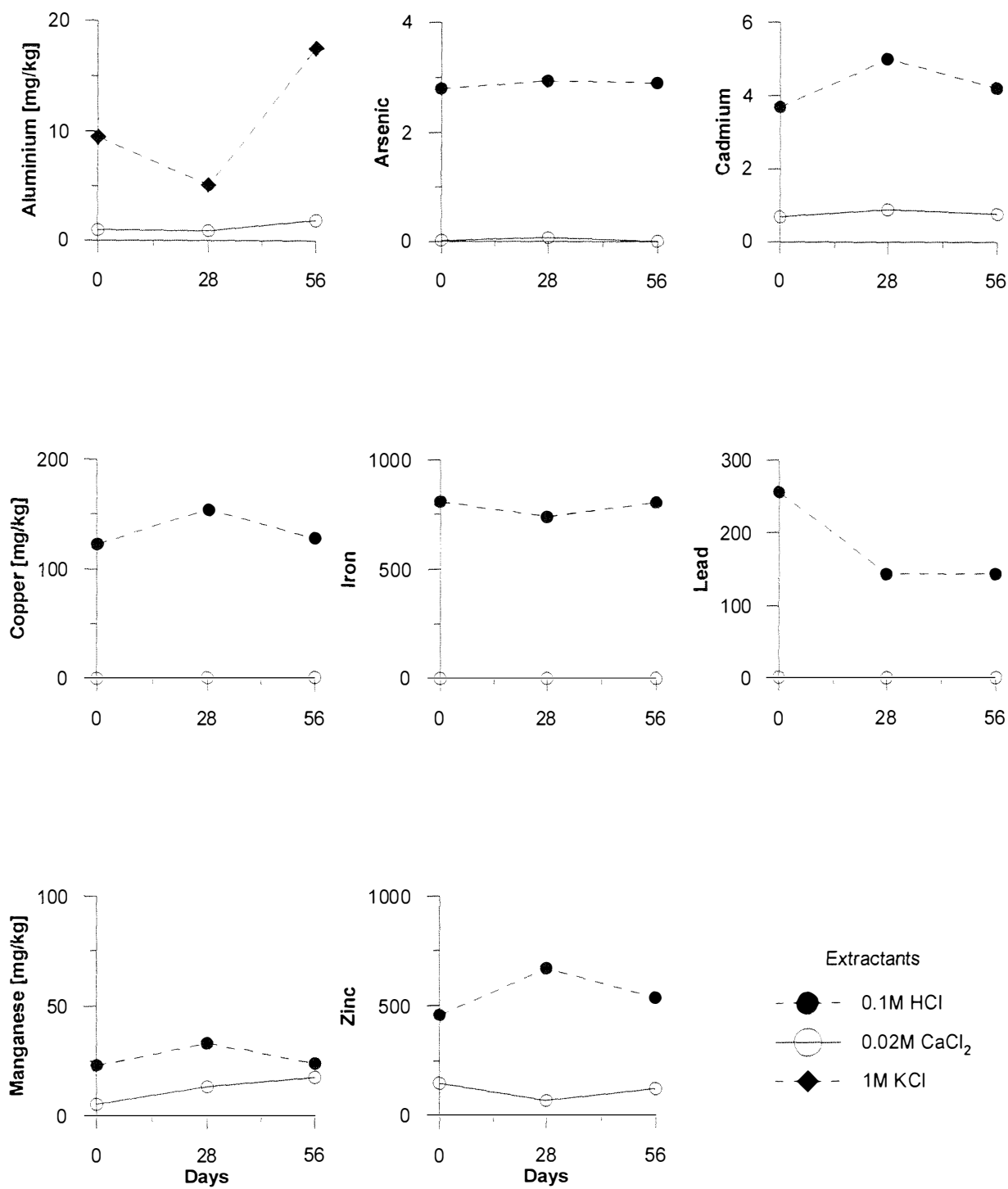


Figure 7.20 Changes in metal concentrations as extracted by 0.1M HCl (●), 0.02M CaCl₂ (o) and 1M KCl (◆) for 440 Mg/ha sludge treated tailings during the growth period.

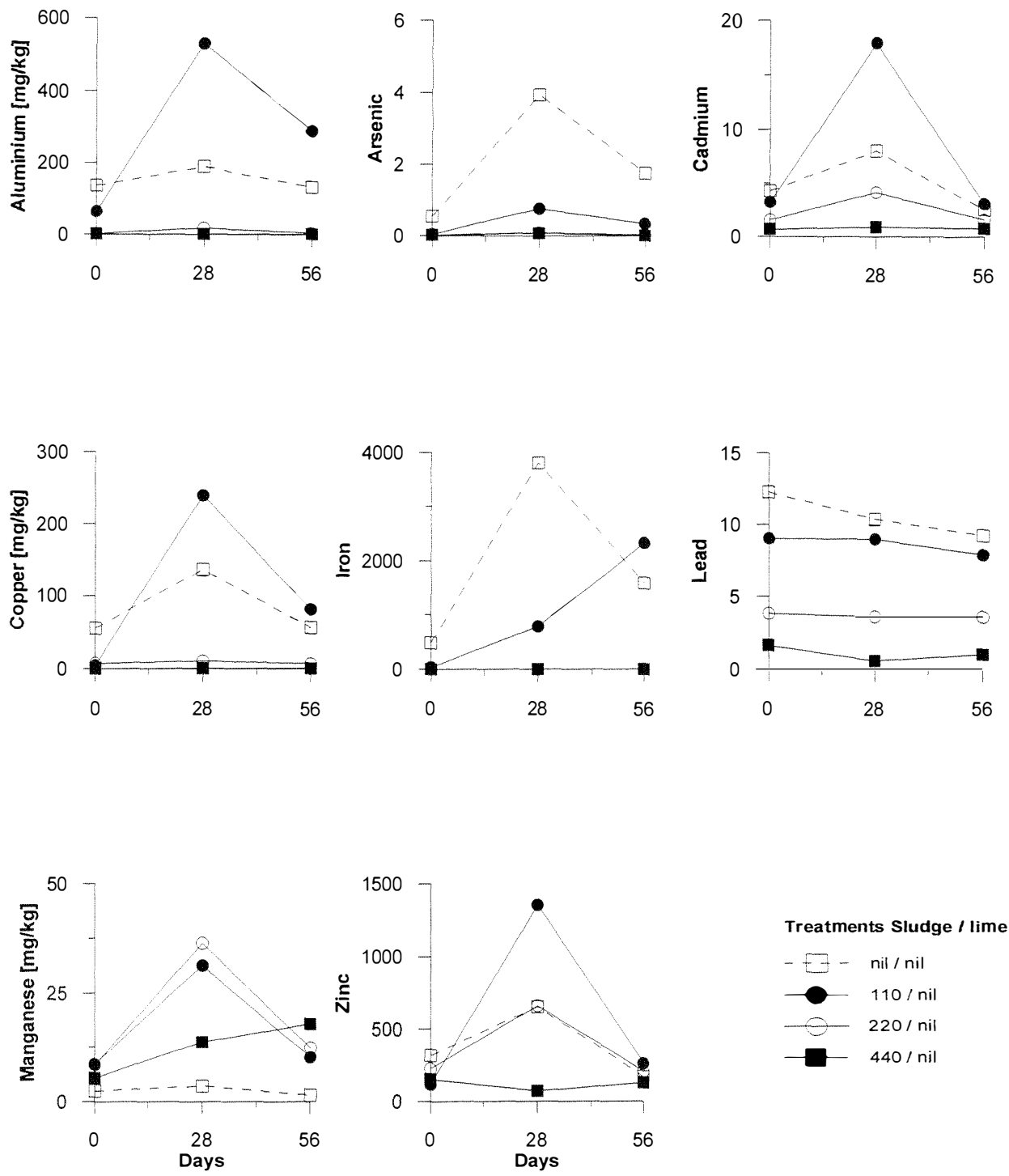


Figure 7.21 Concentrations of various metals extracted by 0.02M CaCl₂ at specified rates of sludge.

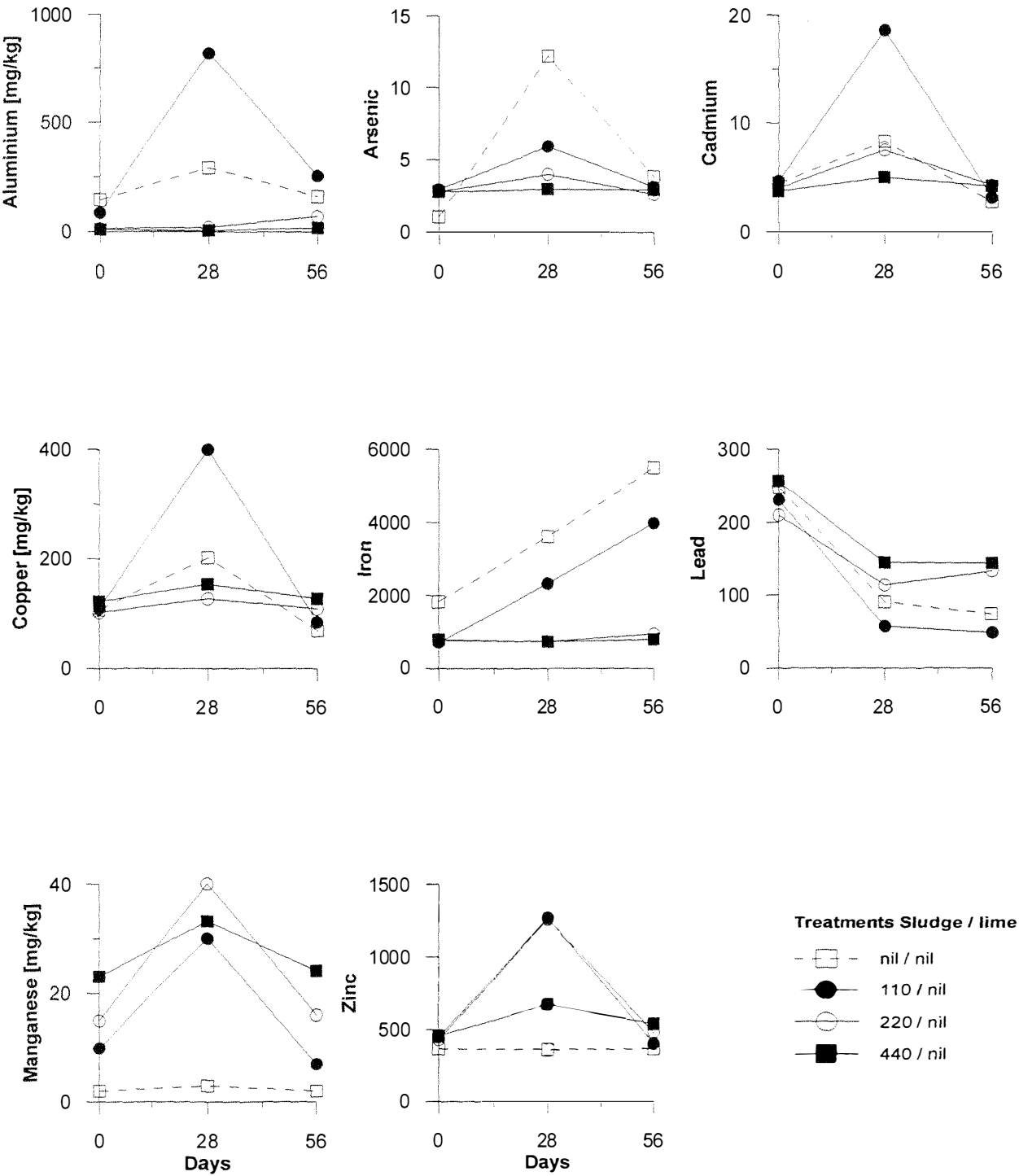


Figure 7.22 Concentrations of various metals extracted by 0.1M HCl at specified rates of sludge

7.7.6.2 Limed Treatments

The addition of lime to the sludge amended tailings was found to greatly improve the overall performance of Merlin, particularly in the nil, 110 and 220 Mg/ha sludge treatments (Figure 7.15b). A positive and highly significant ($P < 0.001$) correlation between dry matter yields and sludge/lime addition was identified. Average dry matter yields were found to increase from 0.62 ± 0.2 g per pot in the nil sludge treatment to over 3.2 ± 0.2 g per pot at the highest sludge rate (Figure 7.15b; Plate 7.8). ANOVA, however, indicated that the increase in dry matter yield between the nil and 110 Mg/ha sludge treatments was insignificant ($P > 0.05$). Merlin yields were, however, significantly higher on limed treatments that were amended with sludge at rates ≥ 220 Mg/ha.

Comparison of Figures 7.15a and 7.15b indicates that the addition of 5.1 Mg/ha of lime to the 440 Mg/ha sludge treated tailings did not substantially improve the performance of Merlin in terms of dry matter production. Lime treated pots yielded an average of just 0.3 grams additional dry matter per pot. Analysis of sown pots at the end of the growing period also indicated that there was little difference between the pH of limed and non-limed 440 Mg/ha sludge treatments (Table 7.14). The availability of metals (as determined by extraction with 0.1M HCl, 1M KCl and 0.02M CaCl_2) were similarly, comparable between the two treatments (Figures 7.20 & 7.26).

In comparison to Merlin the performance of Lotus on the limed treatments was poor. Although lime addition enabled Lotus to ‘successfully’ germinate and establish on 3 of the 4 treatments, dry matter yields of Lotus were significantly ($P < 0.001$) lower than those of Merlin (Figure 7.15b; Plate 7.9). Despite the addition of lime at a rate equivalent to 10.1 Mg/ha complete Lotus die-back again occurred on the 110 Mg/ha sludge treatment (Plate 7.9). The addition of lime and sludge at rates of 8.5 and 220 Mg/ha respectively, similarly failed to significantly improve the establishment and growth of Lotus. Replicate pots sown with Lotus yielded an average dry matter weight of just 0.03 ± 0.03 g on the 220 Mg/ha (limed) sludge treatment. This compares poorly with Merlin which on the same treatment yielded 2.38 ± 0.13 g/pot (70 times the dry matter).

The poor performance of Lotus on all treatments (both limed and non-limed) is believed to reflect the relative intolerance of this species to adverse (highly acidic and/or metal contaminated) growing conditions. Most Lotus plants that established on the various treatments showed signs of chlorosis which suggests that the adverse growing conditions were affecting the plants’ ability to take up N or fix N₂. Foliar analysis conducted in Trial One on Lotus herbage derived from the lime treated tailings indicated that N deficiency was affecting Lotus growth despite the application of what were considered to be adequate quantities of readily available N (Table 7.10).

(i) pH

The pH of the various limed sludge treatments were clearly not maintained at a level conducive to plant growth for the duration of the growing period (Figure 7.16b). Although the four liming rates (Table 7.12) were all found to initially increase the pH of the various sludge treatments to approximately 6.0 as desired, the pH of 3 of the 4 treatments started to decrease almost simultaneously at the end of the pre-sowing incubation period (Figure 7.16b). Although little pH differentiation between some sludge treatment control pots is evident in Figure 7.16a at the end of the growing period, appreciable differences in pH were noted among the sown pots (Table 7.14)

Table 7.14 Average pH of sown pots at week 11 (termination) of trial

Limed Sludge Rate [Mg/ha]	Non-Limed Pots	Limed Pots
nil	2.22 ± 0.02	6.56 ± 0.10
110	2.22 ± 0.03	4.36 ± 0.16
220	3.78 ± 0.35	4.73 ± 0.14
440	4.71 ± 0.05	4.98 ± 0.06

In contrast to the sludge amended treatments, the pH of the treatment that received lime only (16.5 Mg/ha) remained elevated and relatively steady throughout the 24 week monitoring period (Figure 7.16b). This treatment (which was effectively replicated in Trial One), however, demonstrated that far from optimal growth was achieved when the tailings were amended with lime only (Figure 7.15b).



Plate 7.8 This photograph was taken 4 weeks after sowing and compares the growth of *Festuca rubra* (Merlin) on tailings amended with 4 rates of sludge (nil, 110, 220 & 440 Mg/ha; left to right) and 4 rates of lime (16.5, 10.1, 8.5 & 5.1 Mg CaCO₃/ha; left to right).



Plate 7.9 This photograph was taken 4 weeks after sowing and compares the growth of *Lotus corniculatus* on tailings amended with 4 rates of sludge (nil, 110, 220 & 440 Mg/ha; left to right) and 4 rates of lime (16.5, 10.1, 8.5 & 5.1 Mg CaCO₃/ha; left to right).

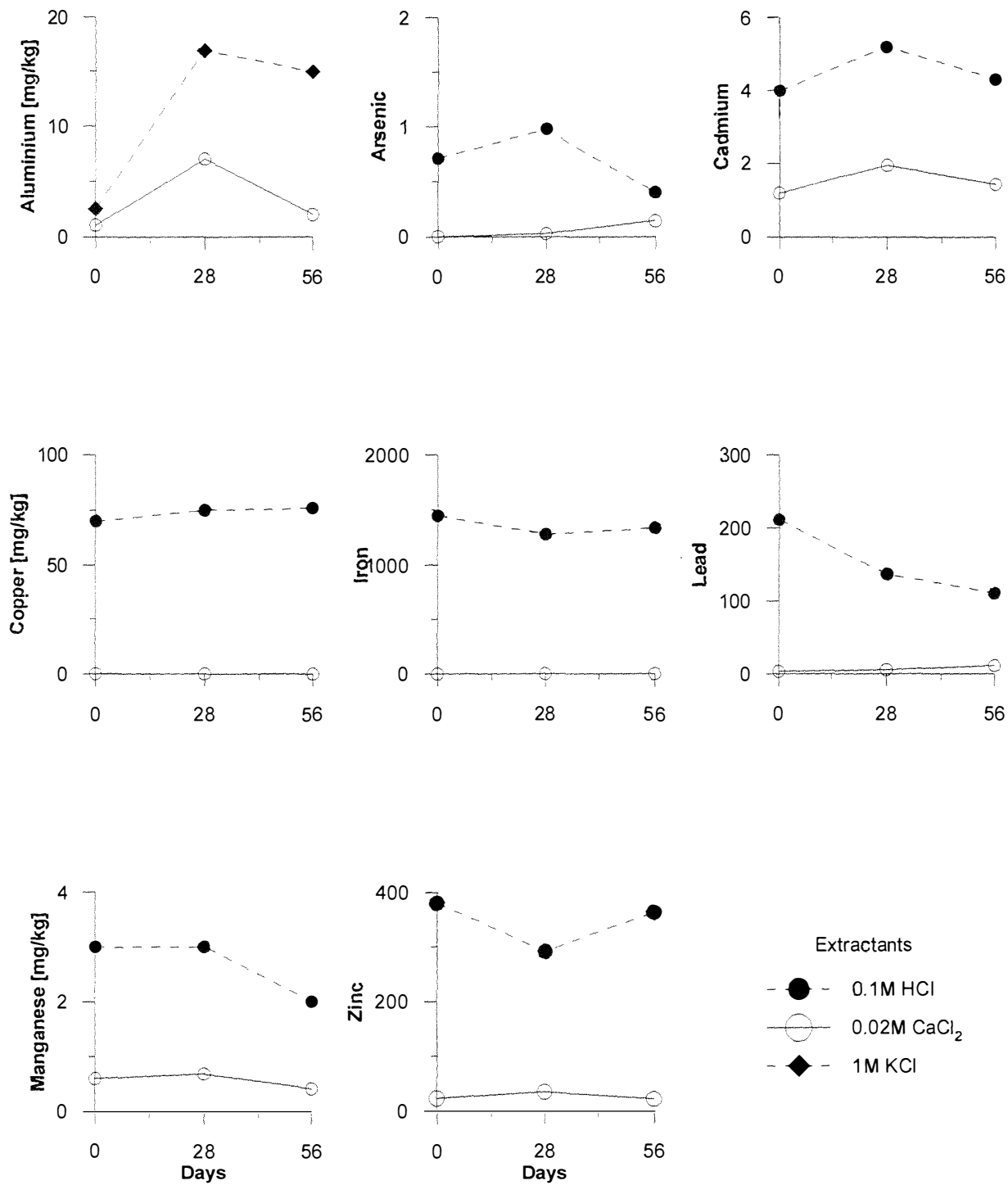


Figure 7.23 Changes in metal concentrations as extracted by 0.1M HCl (●), 0.02M CaCl₂ (o) and 1M KCl (◆) for limed, nil treated tailings during the growth period

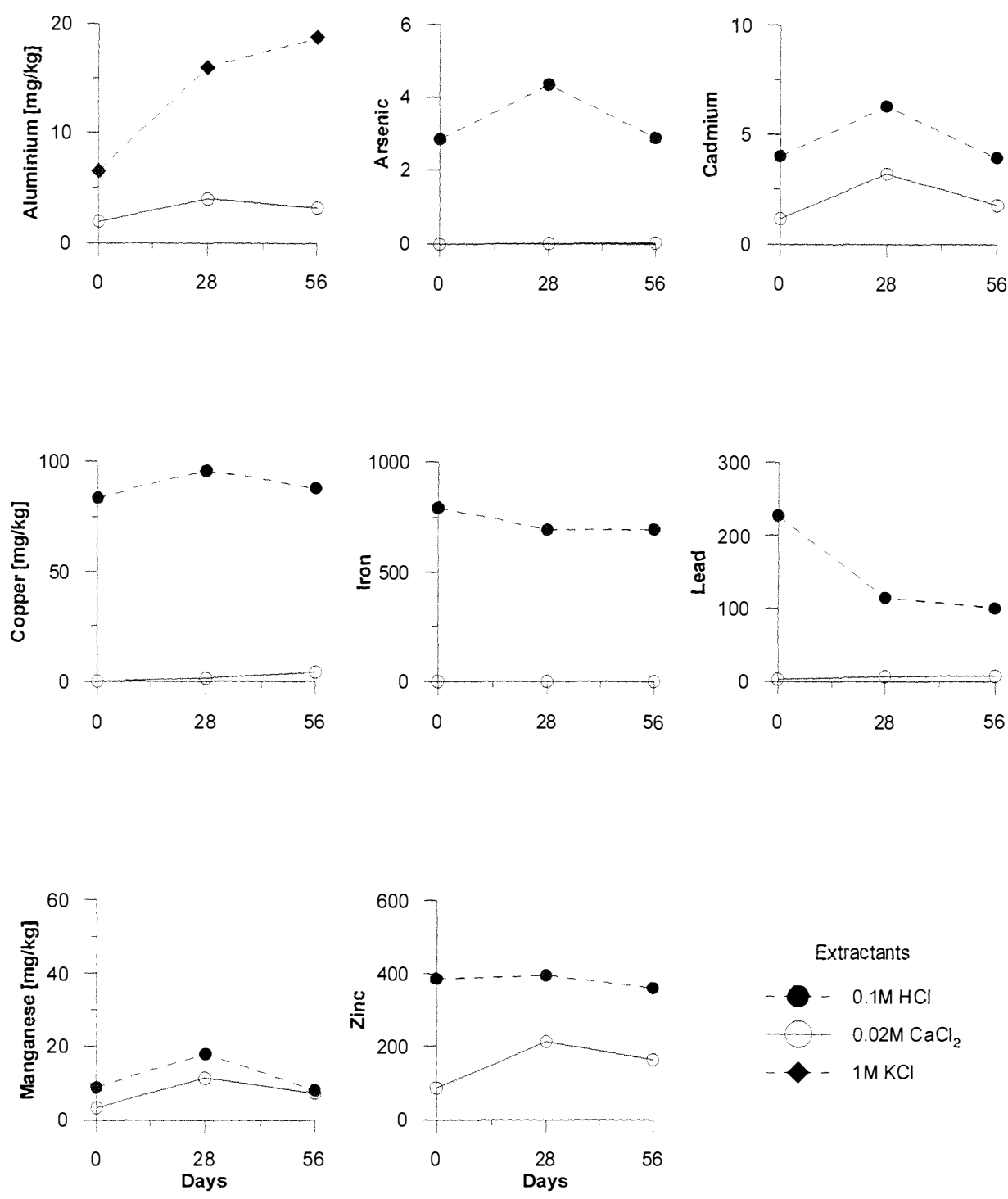


Figure 7.24 Changes in metal concentrations as extracted by 0.1M HCl (●), 0.02M CaCl₂ (o) and 1M KCl (◆) for limed, 110 Mg/ha sludge treated tailings during the growth period

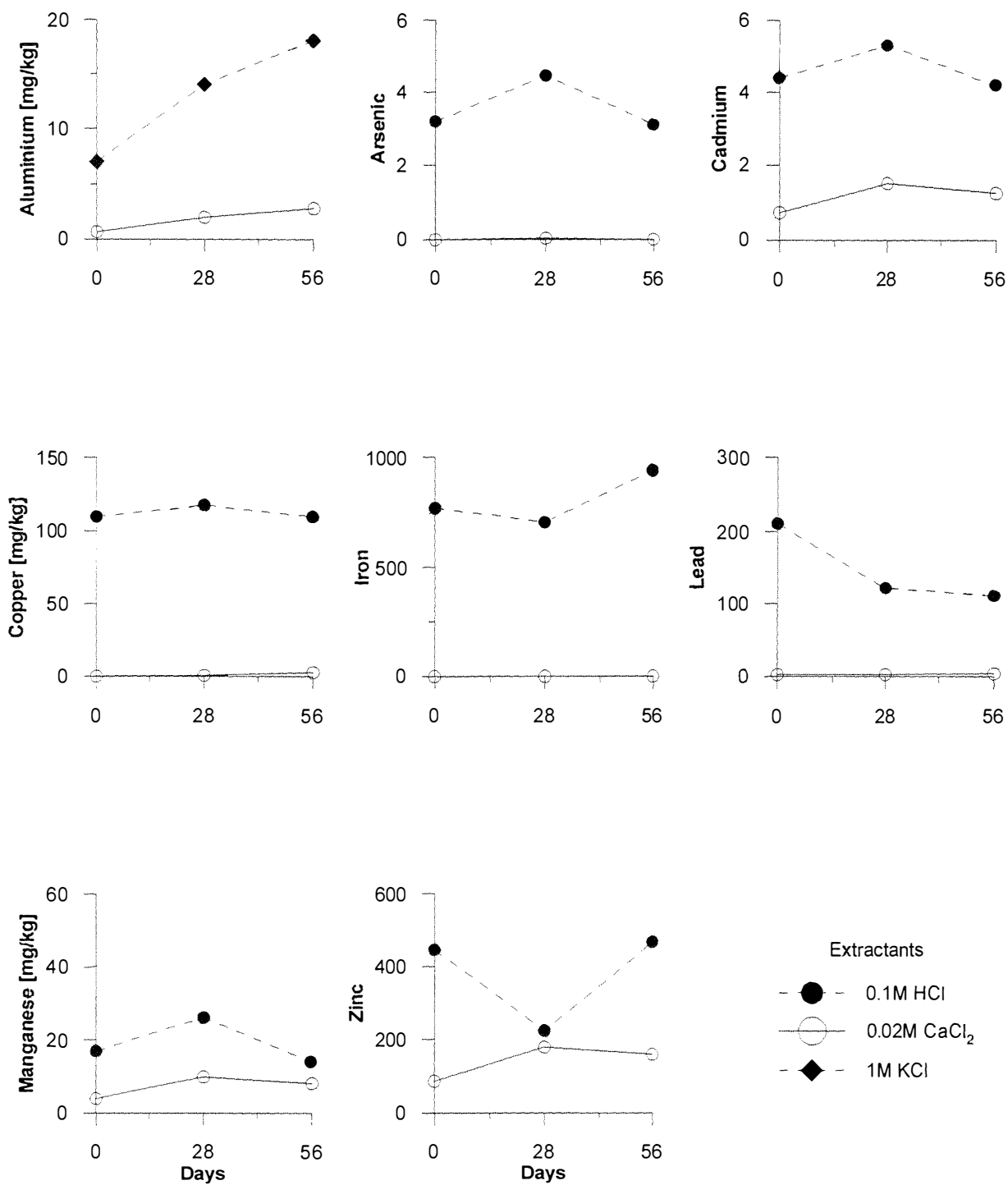


Figure 7.25 Changes in metal concentrations as extracted by 0.1M HCl (●), 0.02M CaCl₂ (○) and 1M KCl (◆) for limed, 220 Mg/ha sludge treated tailings during the growth period

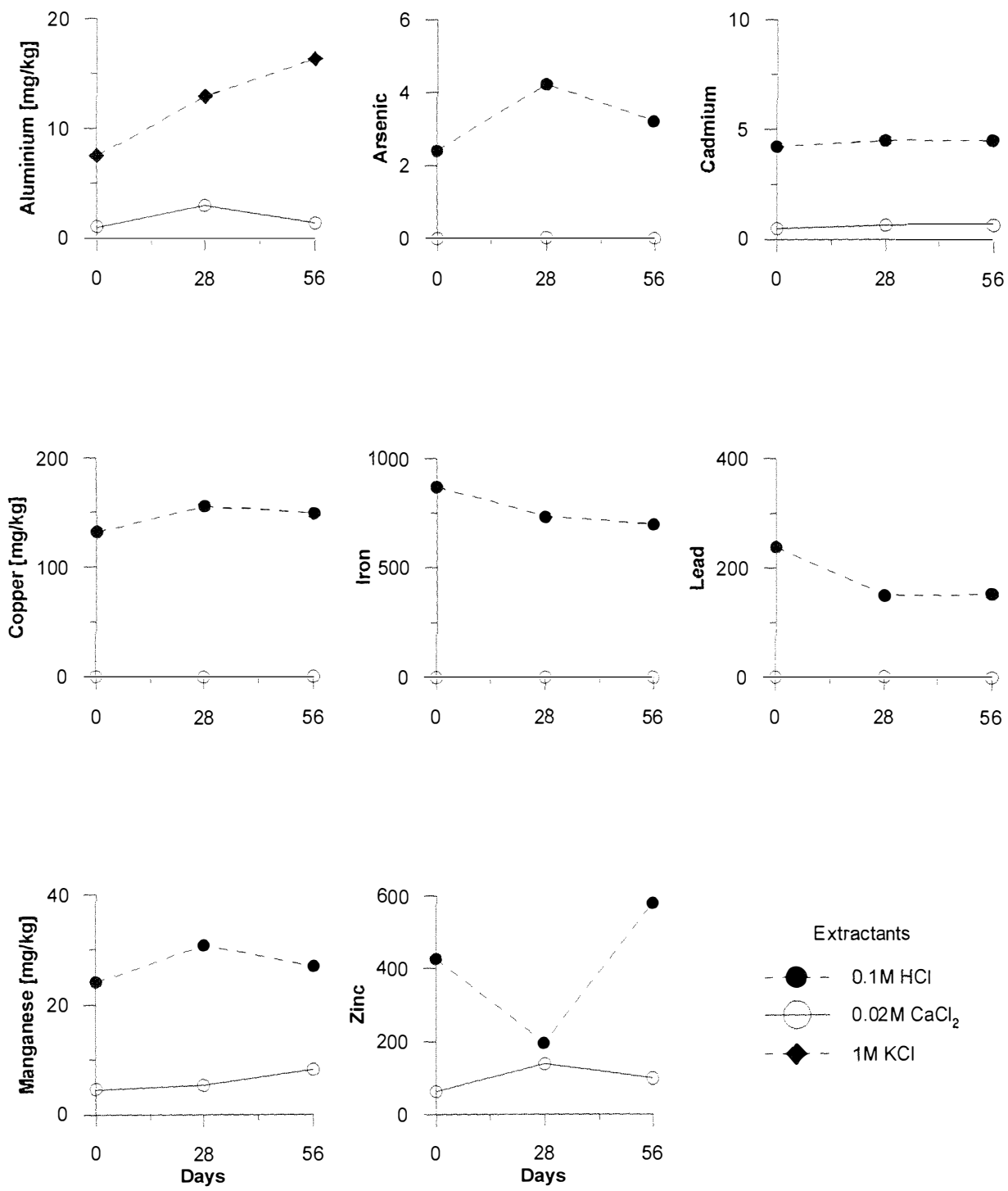


Figure 7.26 Changes in metal concentrations as extracted by 0.1M HCl (●), 0.02M CaCl₂ (○) and 1M KCl (◆) for limed, 440 Mg/ha sludge treated tailings during the growth period

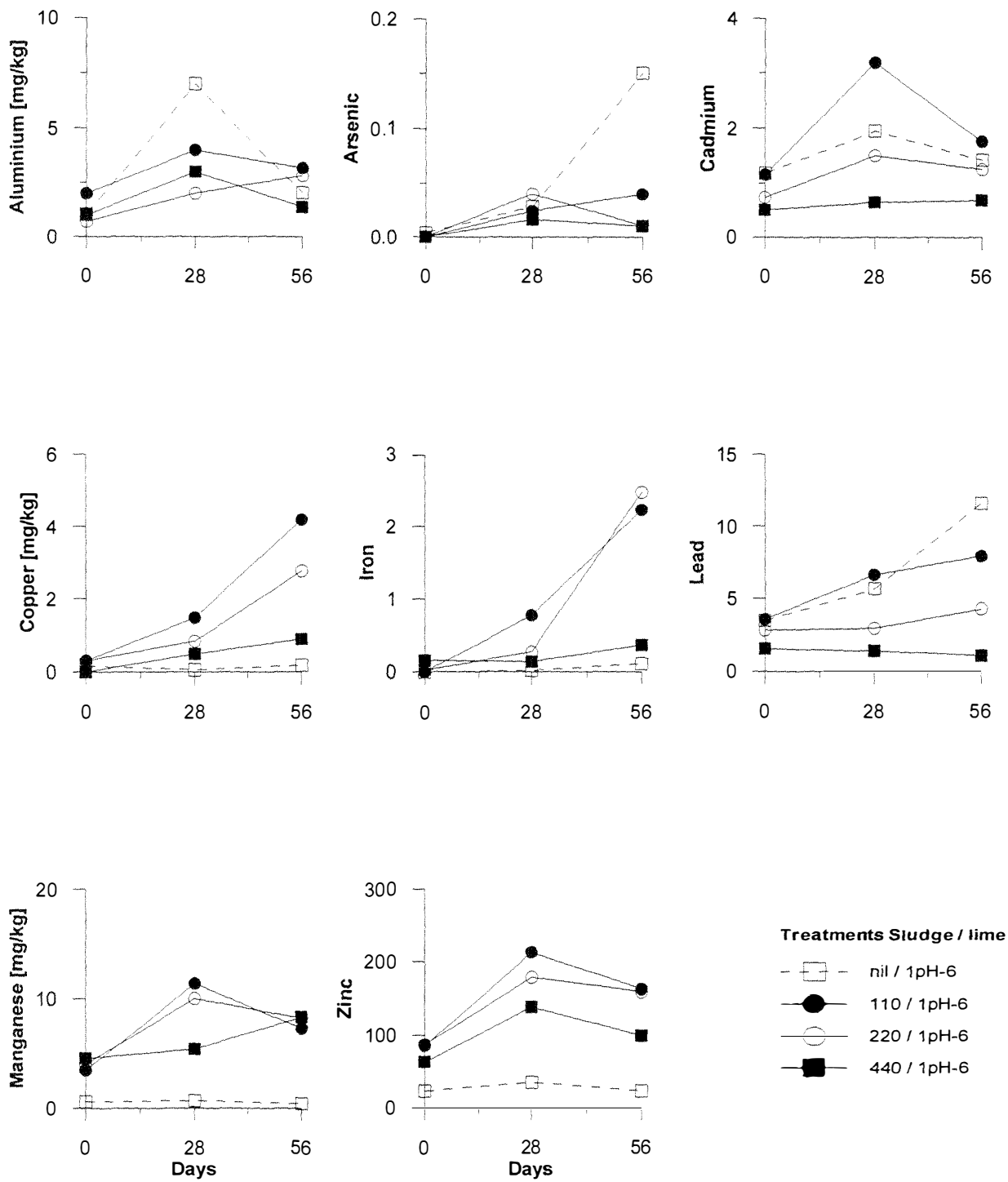


Figure 7.27 Concentrations of various metals extracted by 0.02M CaCl₂ at various rates of sludge treatments which have been limed to pH 6.0.

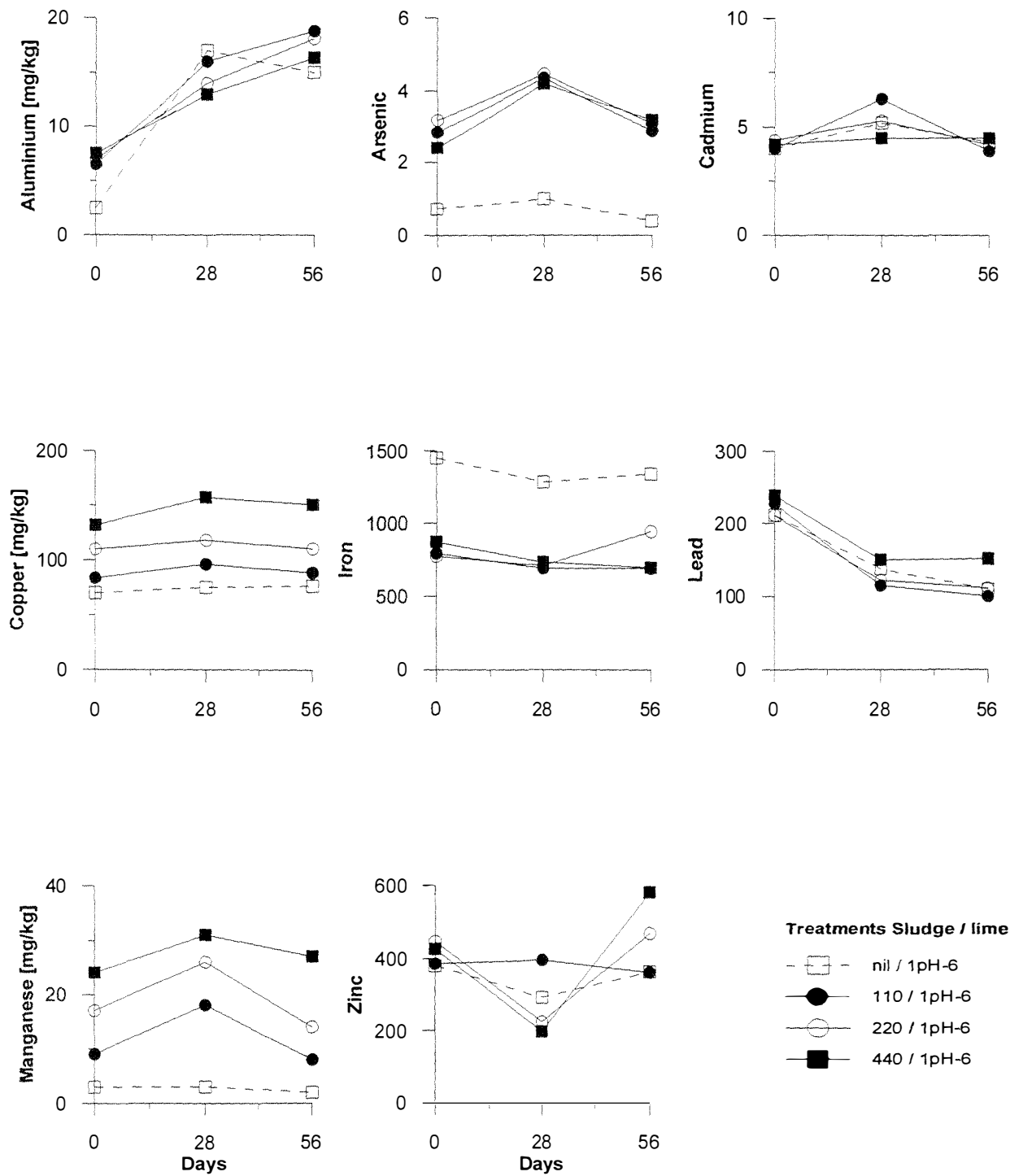


Figure 7.28 Concentrations of various metals extracted by 0.1M HCl at various rates of sludge treatments which have been limed to pH 6.0.

(ii) Extractable Metals

The addition of lime to the various sludge treatments was found to decrease the ready availability ($0.02M$ CaCl_2 extractable) of metals in the amended tailings, particularly in the nil and 110 Mg/ha treatments (Figures 7.23-7.26). Comparison of Al, Cu and Zn levels 4 weeks after sowing in the 110 Mg/ha treatment for example, indicates these metals were reduced from 531, 240 and 1353 mg/kg in the non-limed pots to 4, 1.5, 211 mg/kg respectively in the limed pots (Figures 7.18 & 7.24). The decrease in metal availability was least marked in the 220 and 440 Mg/ha sludge treatments but still appreciable (Figures 7.25 & 7.26). Comparison of Figures 7.21 and 7.27 clearly indicates that the addition of lime reduced metal concentrations and variability between availability of metals between the treatments, particularly in the cases of Al, Cu, Fe and Zn. In several instances the $0.1M$ HCl extractable levels were also substantially reduced (Figure 7.28). Comparison of Figures 7.22 and 7.28 indicates that liming notably reduced the quantity of Al, Cd, Fe and Zn extracted in most treatments.

(iii) Nutrients

Soil chemical analysis of control pots again indicated that sludge addition substantially increased the tailing's nitrogen (N) and phosphorus (P) reserves (Table 7.15). Total P levels were again increased from very low concentrations in the non-sludge amended tailings to very high levels in the 220 and 440 Mg/ha sludge treatments. At the 440 Mg/ha sludge rate total N levels in the amended tailings were approaching those typically found in soils (Table 7.15). Liming appeared to have little effect on the availability of Olsen P levels which were similar albeit slightly lower than levels in the non-limed treatments (Table 7.13).

Levels of exchangeable calcium were predictably higher in all limed treatments. Exchangeable K and Mg levels were found to increase slightly with sludge addition. In contrast to Mg levels which decreased during the course of the trial, K levels were found to increase slightly during the growth period. Sodium levels were not notably effected by the combined application of sludge and lime (Table 7.15). The CEC of the various limed-treatments was found to increase slightly with increasing sludge addition.

Table 7.15 Soil fertility parameters of limed control pots determined at sowing (Week 3) and at the end of the growing period (Week 11). Medium values for New Zealand soils are based on the data of Blakemore *et al.* (1987). *Values are expressed as mg/kg. † Values expressed as meq/100g . nd = not determined

Soil Parameter	Medium Values	Sludge Application Levels [Mg/kg]							
		nil		110		220		440	
		Week 3	Week 11	Week 3	Week 11	Week 3	Week 11	Week 3	Week 11
pH	5.3-6.5	6.91	6.46	6.18	4.30	6.00	4.37	5.71	4.87
Olsen P*	20-30	4.5	2.0	31	27	52	58	70	86
Total P*	400-800	nd	102	nd	569	nd	1174	nd	2302
Total N*	3000-6000	nd	13.0	nd	467	nd	1282	nd	2654
Sulphate*	15-50	1770	1910	1485	1809	1470	2111	1500	2111
Exch. Ca [†]	5.0-10.0	12.9	12.0	12.7	11.5	15.8	13.6	17.4	16.5
Exch. K [†]	0.5-0.8	0.02	0.14	0.08	0.15	0.04	0.17	0.09	0.20
Exch. Na [†]	0.3-0.7	0.1	0.1	0.2	0.1	0.2	0.2	0.2	0.2
Exch. Mg [†]	1.0-3.0	0.17	0.12	0.46	0.31	0.58	0.44	0.90	0.75
CEC [†]	12-25	nd	13	17	16	21	20	24	23

7.7.7 Conclusions of Trial Two

- A ‘satisfactory’ cover of Merlin was established on the non-limed 440 Mg/ha sludge treatment. Below this rate, however, Merlin either failed to germinate (nil and 110 Mg/ha sludge treatments) or seedlings died-off during the growing period. The addition of lime to the various sludge treatments facilitated the establishment of Merlin on all limed treatments.
- Whilst moderate germination rates were attained for Lotus on all treatments (bar that which received no lime nor sludge), this species performed very poorly on both the limed and non-limed sludge treatments in terms of dry matter yield produced. In the non-limed treatments, Lotus in fact failed to produce any dry matter at all and although small yields of Lotus were attained from 3 of the 4 sludge treatments that were limed, the established plants were clearly unhealthy and showed symptoms of metal toxicity and/or nutrient imbalance.
- As the sludge to lime ratio increased so too did Merlin dry matter yields. The positive effects of increasing this ratio is believed to reflect an improvement in the physico-chemical properties of the amended tailings. Specifically it appears that sludge rates of 440 Mg/ha (both with or without the addition of lime) were capable of maintaining

the pH at a level more conducive to nutrient uptake while simultaneously ensuring metal concentrations were sufficiently low in the tailings solution to facilitate the growth of metal-tolerant Merlin.

- The treatment of the tailings with 110 Mg/ha of sludge, either with or without the addition of lime (10.1 Mg/ha), failed to facilitate the establishment of Lotus. Whilst Merlin established on the limed treatment, the level of growth was not significantly greater than that treated with lime only (16.5 Mg/ha). In the absence of lime, the addition of 110 Mg/ha sludge increased the already high availability of some metals in the tailings.
- The significantly higher yields of Merlin obtained from the limed 220 and 440 Mg/ha rate indicate that growth conditions are superior in high sludge to lime ratio treatments. Results from this trial clearly indicate that whilst the application of lime at a rate equivalent to 16.5 Mg/ha may facilitate the growth of plants, the resulting physico-chemical conditions are far from optimal in terms of potential production, particularly in the case of Merlin.
- It is evident that a satisfactory cover of Merlin is attainable through the amendment of tailings with the equivalent to 440 Mg/ha of North Shore sewage sludge. The results of this trial indicate that this treatment may inhibit severe acidification of the tailings and facilitate plant growth for at least 24 weeks.

7.8 Chapter 7 Summary & Conclusions

To briefly summarise the conclusions of the plant growth trials (see sections 7.66 and 7.77), it is evident that on tailings treatments sown with metal-tolerant varieties of *F.rubra* or *A.capillaris*, satisfactory cover was achieved by the addition of lime at a rate of 16.5 Mg/ha (1 pH-6 rate) or composted sewage sludge at rates ≥ 220 Mg/ha. On the lime amended tailings metal-tolerant plant taxa were found to substantially out yield their non-metal-tolerant counterparts. Whilst plants were at least temporarily established on lime amended tailings, dry matter yields were relatively much lower than on treatments receiving high rates of sludge. The addition of lime at a rate of 112 Mg/ha (TAGP rate) was found to detrimentally affect plant growth due to pH-induced nutrient deficiencies. In contrast, plant growth improved significantly with increasing sludge addition.

CHAPTER 8

Thesis Summary & Conclusions

8.0 Introduction

The primary objective of this thesis was to determine the potential for revegetating the Tui mine tailings. To achieve this objective the relevant literature was reviewed, the tailings were physically and chemically characterised, small scale incubation and plant growth experiments were developed and conducted in the glasshouse and the overall findings discussed. The main conclusions of the literature review and the experimental work are summarised below.

8.1 Literature Review

- The Tui Mine is situated on the flanks of the Kaimai Ranges and was last actively mined between 1967 and 1974. During this time an estimated 163,000 tonnes of base-metal ore was extracted and processed on site. The Tui ore deposits comprised two brecciated quartz reefs which were effectively cemented by an aggregate of sulphide minerals; predominantly sphalerite, galena chalcopyrite and pyrite. The ore also contained appreciable quantities of gold and silver.
- The mining operation generated an estimated 100,000 m³ of sulphide-bearing tailings. These finely-ground tailings are contained in a rudimentary dam located at an altitude of 350 m in one of numerous steep stream valleys which dissect hydrothermally altered andesitic country rocks on Mt. Te Aroha.
- Rainfall at the Tui mine site is high (c. 2000 mm/yr), well distributed but, at times, very intense. The Tui and Tunakohia streams, which flank the Tui mine site, intercept catchment rainfall as well as highly contaminated drainage from the tailings dam and mine adits. The inflow of acid mine drainage (AMD), characterised by low pH and high concentrations of Cd, Cu, Fe, Mn and Zn, has rendered the Tui Stream largely devoid of aquatic life .
- The vegetation type surrounding the mine site is predominantly dense, secondary native bush which contains a variety of hardwood species. The ground cover is dominated by mosses and ferns which testify to the moist conditions prevailing at the site.

- The Matamata-Piako District Council and the Department of Conservation, who currently own the Tui mine site, are responsible for mitigating environmental problems generated by the past mining operation.
- Literature pertaining to mine site degradation and reclamation indicates that the certain problems encountered at the Tui mine site, including the generation of AMD and the scarcity of vegetation on disturbed areas, are common features of abandoned mine sites where sulphide-bearing mine wastes have been excavated and left exposed to the atmosphere.
- The severe acidification of mining wastes and the concomitant release of AMD are problems most likely to arise from materials which have a high pyrite to carbonate mineral ratio and are situated at sites where moist, well aerated and warm conditions prevail. Such conditions will generally facilitate abiotic pyrite oxidation at circumneutral pH and biologically catalysed oxidation under extremely acidic conditions ($< \text{pH } 3.0$).
- Whilst a wide range of technologies exist to treat metal contaminated mine drainage (including AMD), the most promising systems in terms of cost and ongoing maintenance appear to be passive water treatment systems. These systems exploit natural processes, that occur in aerobic and anaerobic wetlands, to precipitate and complex heavy metals. Anoxic Limestone Drains (ALDs) may be used, in conjunction with wetlands, to increase the bicarbonate alkalinity and pH of drainage waters and to ultimately reduce acidity and metal loading.
- Preventative rather than palliative measures are, however, widely recognised as being more effective means of combating sulphide oxidation and AMD generation. Low permeability capping materials combined with surface vegetation are common methods used to prevent or reduce sulphide oxidation and to improve the aesthetic value of degraded mine sites.
- Previous research indicates that the addition of liming agents and/or organic wastes to sulphide generating materials may not only serve to ameliorate growing conditions but may also retard the rate of pyrite oxidation and thus inhibit the onset or continued generation of AMD.
- In circumstances where lime is added to sulphide-bearing material intended for use as a 'surrogate soil', the material's inherent Acid Generating Potential (AGP) must be evaluated to ensure that sufficient lime is incorporated to prevent rapid

reacidification of the material. Whilst numerous methods have been developed to assess the AGP of mining wastes, there is currently no universally accepted method.

- Although literature pertaining to the reclamation of colliery wastes is abundant, comparatively little literature exists that specifically discusses the characterisation and reclamation of base-metal tailings.

8.2 Characterisation of the Tui Mine Tailings

- Physical characterisation of the Tui tailings using laboratory and field based measurements indicated that whilst they are not an optimal plant growth medium, they pose no major physical limitations to plant growth. Poor aeration and susceptibility to erosion are, however, problems that could potentially affect establishing plants in certain areas of the dam.
- In terms of their chemical properties, the tailings in their unamended state were identified to be an extremely hostile plant growth medium. The tailings' very low pH combined with their high base-metal content are the two main factors inhibiting plants from colonising the site. Growing conditions within the tailings are further exacerbated by their negligible organic matter content and low clay content.
- Elemental analysis of the tailings indicated that both the total and labile (0.1M HCl extractable) metal contents of the tailings are spatially highly variable. Metal concentrations were also found to vary substantially with depth.
- With the notable exception of Pb, the concentrations of most metals were found to dramatically increase below about 200 mm depth. Accordingly, total sulphur levels and the theoretical AGP of the tailings also increased with depth as sulphide mineral concentrations increased.
- Whilst the surface tailings (0-200 mm) were found to contain relatively low concentrations of sulphide minerals, it is estimated that a liming rate in the vicinity of 50 Mg/ha would be required to prevent long term reacidification of the surface tailings.
- Chemical characterisation of the tailings indicated that, in terms of their AGP and metal content, the surface tailings (0-200mm) are far better suited for use as a growing medium than tailings obtained from deeper within the profile. Plants, however, are not envisaged to begin colonising the tailings until the adverse chemical growing conditions are ameliorated via some form of amendment(s) which would

have to simultaneously provide nutrients, increase pH and reduce metal bioavailability.

- XRD analysis of the Tui mine tailings showed that they comprise primarily quartz with subordinate kaolinite and pyrite. Fractionation of the tailings using a solution of sodium polytungstate (density = 2.8 g/cm³) facilitated the detection of small but appreciable quantities of sulphide minerals such as anglesite, chalcopyrite, galena and sphalerite in most samples.
- The mass of the heavy mineral fraction of the Tui tailings was found to significantly increase with depth from about 1.5% at 0-100 mm depth to more than 16% at 500-600 mm depth.
- The detection of highly insoluble PbSO₄ (anglesite) in the tailings samples provided a ready explanation for the presence of very high total Pb concentrations in surface 200 mm of the profile where other heavy metals were contrastingly found in relatively low concentrations.
- XRD results substantiate the findings of the chemical characterisation that surface tailings (0-200 mm) have been extensively oxidised. Evidence includes; (i) the increasing proportion of heavy minerals with depth, (ii) the lower levels of XRD-detectable sulphide minerals in the surface tailings and (iii) the presence of relatively high concentrations of secondary anglesite in the surface tailings.
- SEM images of remnant sulphides isolated in the Tui tailings provided further evidence that the surface tailings (0-200 mm) have undergone extensive weathering. Sulphide minerals isolated from this zone were characterised by their craggy and highly irregular shape indicating that they have been extensively weathered via oxidation. In contrast, sulphide minerals obtained from deeper within the profile generally exhibited highly angular, and in some instances cubic morphology, characteristic of unaltered pyrite and other sulphide minerals
- Based on SEM and EDS analysis it is thus postulated that the original distribution of base-metals within the Tui tailings profile was relatively uniform with depth and that the depletion of Cu, Fe and Zn in the surface tailings (0-200 mm) has resulted from the oxidation of remnant sulphide minerals within this relatively well aerated zone and the subsequent dissolution and leaching of weathering products.
- Analyses conducted using EDS support XRD findings which indicate that the Tui tailings comprise primarily quartz but in addition contain a variety of heavy metal-

bearing minerals. The processing of the Tui ore, however, has selectively enriched the tailings with pyrite. Relatively high concentrations of pyrite persist below 200 mm depth and form a significant source of potential acidity.

- The results of a lime incubation trial conducted over a 1½ years period confirmed that the uppermost tailings sample assessed (0-100 mm) had very low AGP and that the sample's pH was readily maintained at circumneutral levels via the addition of relatively low rates of lime.
- Tailing samples obtained from below 100 mm depth, however, were found to reacidify within a year when amended with lime at rates based on those required to raise the pH of the tailings to approximately 6.0 (1 pH-6 liming rate). Two or four times the 1 pH-6 liming rate were required to prevent reacidification of subsurface tailings over the trial period.
- Contrary to estimated TAGP values, which indicated that tailings obtained from between 500-600 mm were likely to be the most reactive (in terms of acid generation and metal liberation), the incubation study suggested that samples obtained from between 200 and 400 mm depth were most reactive. The greater reactivity of these samples under aerobic incubations conditions (considered to be conducive to the biochemical oxidation of sulphides) is attributed to their appreciably finer grain-size and hence larger reactive surface area.
- Whilst high rates of lime were generally found to decrease the availability of labile heavy metals in the tailings, the lowest rate in contrast was found to increase the availability of Cu, Pb and Zn in the tailings and hence exacerbate potential growing conditions. The availability of H^+ , $SO_4^{=}$ and soluble Fe was generally greater in samples treated with the ½ pH-6 liming rate than in the control samples. This finding has important implications for reclaiming the Tui mine sites as it indicates that the application of rates of lime below a certain threshold level may in fact enhance sulphide oxidation rates and further degrade growing conditions.

8.3 Plant Growth Trials

- The failure of all plant taxa (including metal-tolerant varieties) to germinate on fertilised but otherwise unamended Tui tailings confirmed that the tailings are an extremely hostile plant growth medium. Extreme acidity and the high availability of

phytotoxic metals (Al, Cu, Fe and Zn) were considered to be the primary factors inhibiting germination.

- The addition of a 'low' rate of lime (8.25 Mg/ha) to the tailings, however, was not found to substantially improve growth conditions. To the contrary, it was found to increase the relative bioavailability of some metals as the tailings re-acidified. This finding is consistent with observations made in the lime incubation trial.
- The addition of lime at rates equivalent to 16.5 Mg/ha (1 pH-6 rate) or 112 Mg/ha (TAGP rate) facilitated germination and plant growth of all taxa by reducing the pH and bioavailability of metals in the tailings. Substantially greater mean yields were, however, obtained on tailings amended with the lower of these two liming rates; a finding that is attributed to the adverse effects of the very high liming rate on plant nutrition and particularly on P uptake.
- Metal tolerant *Festuca rubra* (var. Merlin) was clearly the most successful of the plant taxa trialed in this study in terms of the biomass produced and vigour. Merlin significantly out-yielded the non-metal-tolerant variety of *F.rubra* (var. Lobi) at both effective liming rates. A significant difference in yield between the metal-tolerant and non-metal-tolerant *Agrostis capillaris* cultivars was noted only at the lowest effective liming rate (1 pH-6 rate). At the higher liming rate both cultivars of *A.capillaris* performed very poorly. Rhizobial inoculation of *Lotus corniculatus* failed to significantly improve this species' poor performance at both liming rates.
- Attempts to establish plants on the lime amended (and fertilised) tailings clearly demonstrated that the liming requirements of the Tui tailings (in terms of optimising plant growth) is a trade-off between diminished plant response resulting from the application of high rates of lime and the need to ensure that sufficient lime is added to prevent reacidification of the growing medium.
- The amendment of the tailings with various rates of composted sewage sludge and lime did little to improve the growth performance of *L.corniculatus*. This species failed to establish on all non-limed sludge treatments. In the case of *F.rubra* var. Merlin, however, very satisfactory plant growth was attained on 440 Mg/ha sludge treatments both with or without the addition of lime. Satisfactory Merlin growth was also achieved on 220 Mg/ha sludge treatments where lime was added.
- The satisfactory performance of Merlin on treatments amended with high rates of sludge is believed primarily to reflect the ability of sludge to:- (i) supply plant

nutrients, particularly N & P, (ii) increase and maintain pH at levels more conducive to the growth of plants, (iii) reduce the bioavailability of heavy metals and (iv) improve the physical characteristics of the rooting medium.

- Results from the plant trials clearly indicate, that whilst the application of lime at a rate equivalent to 16.5 Mg/ha may facilitate the growth of plants, the resulting physico-chemical conditions are far from optimal in terms of potential production, particularly in the case of Merlin. It is evident that much better Merlin establishment was attained through the amendment of tailings with high rates of composted sewage sludge.

8.4 Overall Conclusion

Based on the information presented in this thesis, it is evident that the Tui mining operation was conducted in an extremely sensitive mining environment. Environmental degradation was exacerbated at the site by the failure of the mining company to implement what would now be considered to be very rudimentary measures to minimise environmental degradation. Characterisation of the tailings, that were effectively dumped at the processing site, indicate that they are chemically very poorly suited to plant growth due to their very low pH, high content of phytotoxic metals and their potential to generate further acidity through sulphide oxidation. Whilst very high levels of acid generating sulphide minerals were found to persist in the tailings below 200-300 mm depth, it was demonstrated that plants can be established on the highly weathered surface tailings (0-200 mm) via the application of sludge and/or lime under controlled conditions. The usefulness of amending the tailings with a source^{of} organic matter and utilising metal-tolerant plant species to revegetate the tailings was clearly demonstrated by the results of plant growth trials. It is envisaged that unless attempts are made to reclaim the site, sulphide oxidisation and concomitant acid generation and metal liberation will continue to contaminate ground and stream waters indefinitely. The establishment of vegetation on the tailings would, at the very least, serve to physically stabilise the tailings and improve the aesthetic value of the site.

8.5 The Scope for Future Work

Whilst the research presented in this thesis adds to our 'reclamation knowledge base' by elucidating environmental problems at the Tui mine site and by providing insight into

the viability of revegetating the tailings, by its very nature it has created niche opportunities for future research. Perhaps the most obvious and important question generated by this study is... “*Can vegetation be established on tailings under the environmental conditions prevailing at the Tui mine site?*” It is envisaged that the next logical step leading on from this study would be to investigate this research question by establishing *in situ* field trials at the Tui mine site. Clearly, the very promising plant growth results obtained in the glasshouse using metal-tolerant *Festuca rubra* in conjunction with high rates of sludge should strongly influence future field trial designs. The incorporation of native plants into such field trials would have obvious merit considering the nature of the vegetation surrounding the tailings dam.

The effects of various surface treatments in terms of their ability to inhibit subsurface sulphide oxidation rates (and ultimately AMD) require investigation. Whilst there is much speculation about the ability of organic matter-based covers to inhibit sulphide oxidation, hard evidence from *in situ* field trial work is scarce. It is envisaged that the use of *in situ* leaching columns and/or vegetated lysimeters may provide an opportunity to investigate the impact of vegetative covers on oxidation rates as well as the possible alteration of chemical and biological processes within the tailings profile.

Other areas of research that require and/or warrant further investigation at the Tui mine site include:-

- The determination of suitable fertiliser regimes for revegetative reclamation.
- The apparent ability of low rates of lime (or sludge) to enhance sulphide oxidation.
- The impact of capillary rise and the effects of a high water table in the field on plant establishment.
- Suitable amendments/strategies for revegetating dam batters.
- Assessment of indigenous metal-tolerant plant species for revegetation.
- Identification of leguminous species tolerant to growing in amended tailings.
- The effectiveness of a capping layer(s) in reducing capillary rise and isolating sulphidic materials from water and oxygen.
- The potential use of passive treatment systems to treat water from the site clearly needs assessing as a part of the overall rehabilitation strategy.

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Appendices

Appendix 4(A) Total Sulphur Determination by Sodium Bicarbonate Fusion (Adapted from Steinbergs *et al.*, 1952)

Reagents

- (i) Oxidising Agent: Mix NaHCO_3 and Ag_2O at 12.5:1 ratio.
- (ii) 5M HCl
- (iii) NaHCO_3

Method

- (i) Grind samples to less than 150 μm .
- (ii) Accurately weigh about 0.25 g of sample into a pyrex tube and add 0.5 g of oxidising agent. Thoroughly mix contents with vortex mixer.
- (iii) Cover resulting mixture in test tube with approximately 0.5 g of NaHCO_3 .
- (iv) Fuse in muffle furnace at 550°C for 3 hours.
- (v) After cooling very slowly add 10 mL of 5M HCl.
- (vi) Mix solution with a vortex mixer and heat solution at 90°C for 1 hour.
- (v) Filter with Whatman No. 41 and quantitatively dilute.

Analysis

- (i) Analyse total sulphur in digest using auto-analyser and methylene blue method of Johnson & Nishita (1952) (Blakemore *et al.*, 1987).

Appendix 4(B)**Calcium Phosphate Extractable Sulphate**

(Adapted from Searle, 1979)

Reagents

- (i) 0.01M $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ solution

Conditions

- (i) Solution to sample ratio 5:1
- (ii) Temperature $20 \pm 2^\circ\text{C}$
- (iii) Period of shaking $\frac{1}{2}$ hour
- (iv) Shaking speed 80-100 rpm

Method

- (i) Weigh 5.0 g of sample into a centrifuge tube.
- (ii) Add 25 mL of phosphate solution to the sample.
- (iii) Shake the solution for $\frac{1}{2}$ an hour in an end of end shaker.
- (iv) Centrifuge at 9000 rpm for 5 minutes.
- (v) Decant solution through Whatman No. 41 filter paper.
and quantitatively dilute samples with phosphate solution.

Analysis

- (i) Analyse phosphate extractable sulphur in the digest using auto-analyser and methylene blue method of Johnson & Nishita (1952) (Blakemore *et al.*, 1987).

Appendix 4(C) Acid Generating Potential (AGP) Based on Sulphur Analysis(Adapted from Sobek *et al.*, 1987).**Method**

- (i) Determine total sulphur content of sample (Appendix 4.1A).
- (ii) Determine phosphate extractable sulphate content of sample (Appendix 4.1B).
- (iii) Estimate % Sulphide S using Equation 1.

$$\text{[Equation 1]} \quad \text{Sulphide S [\%]} = \frac{\text{Total S [mg/kg]} - \text{sulphate S [mg/kg]}}{10,000}$$

Based on the stoichiometry of FeS_2 oxidation a 1000 Mg of a material containing 0.1 % S (all as pyrite) will oxidise to produce a quantity of H_2SO_4 which requires 3.125 Mg of CaCO_3 to neutralise (Sobek *et al.*, 1987). Thus, the AGP of a sample can be calculated using Equation 2.

$$\text{[Equation 2]} \quad \text{AGP [Mg CaCO}_3\text{/1000 Mg of tailings]} = \text{Sulphide S [\%]} * 0.3125$$

Appendix 4(D)**HF/HNO₃ Total Metal Extraction**
(Massey University Soils Dept. Standard Method)**Reagents**

- (i) Concentrated Nitric Acid (HNO₃)
- (ii) Concentrated Hydrofluoric Acid (HF)
- (iii) 2M Hydrochloric Acid (HCl)

Method**Day 1**

- (i) Accurately weigh about 0.1g to 0.2g of air-dry sample into a polypropylene beaker.
- (ii) Add 5 mL of concentrated HNO₃ and leave the beaker to stand in a fume hood for about 1½ to 2 hours.
- (iii) Add 5 mL of concentrated HF acid (40%) and leave the beaker to stand overnight in a fume hood.

Day 2

- (iv) Evaporate the sample to dryness on a water bath at 80°C (approx. 3 hours).
- (v) Add 5 mL of concentrated HF acid (40%) and again take to dryness.
- (vi) Dissolve the residue in 5 mL of concentrated HCl.
- (vii) Make to 100 mL volume in volumetric flask with 2M HCl (rinse beaker residue).
- (viii) Analyse.

Appendix 4(E)**25% (v/v) HNO₃ Pseudo-Total Metal Extraction**
(Adapted from Smith & Bradshaw, 1979)**Reagents**

- (i) 25% v/v HNO₃

Method

- (i) Grind sample to <150 µm (optional).
- (ii) Take 0.5 g of air-dry sample into a 200 mL digestion tube.
- (iii) Add 25 mL of 25% v/v nitric acid and mix thoroughly with vortex mixer.
- (iv) Note total mass, and then cover with small glass funnel.
- (v) Heat the samples for 1 hour at approximately 100°C.
- (vi) Transfer to centrifuge tubes and centrifuge at 9000 rpm for 5 minutes.
- (viii) Filter sample through Whatman No. 41 filter paper.
- (ix) Quantitatively dilute to 100 mL with 1:1 H₂O / HNO₃.
- (x) Analyse.

Appendix 4(F)**0.1M HCl Metal Extraction Procedure**

(Adapted from Viets & Bowen, 1965)

Reagents

- (i) 0.1M HCl

Method

- (i) Accurately weigh a 5.00g air-dry sample into 50-mL polypropylene centrifuge tubes.
- (ii) Add 25 mL of the extractant and shake the samples end-over-end for 16 hours.
- (iii) Remove and centrifuge samples at 9000 rpm for 5 minutes.
- (iv) Filter solutions Whatman No. 41.
- (v) Dilute as necessary and analyse.

Appendix 4(G)**30% H₂O₂ Metal Extraction Procedure**

(Trial Procedure)

Reagents

- (i) 30% Analytical Grade Hydrogen Peroxide (H₂O₂)
- (ii) 0.1M HCl

Method

- (i) Accurately weigh 0.1 to 0.5g air-dry sample into a large wide-mouth conical flask, recording mass of flask.
- (ii) Add 20 mL of H₂O₂ and gently warm on a hot plate until reaction ceases.
- (iii) Add a further 20 mL of H₂O₂ allow reaction to terminate and boil until near dryness.
- (iv) Repeat the above step until no further reaction occurs.
- (v) Take sample to near dryness and gravimetrically readjust extractant volume to 25 mL with 0.1M HCl.
- (vi) Centrifuge sample at 9000 rpm for 5 minutes and filter through Whatman No. 41 paper.
- (v) Dilute as necessary with 0.1M HCl and analyse.

Appendix 4(H) Theoretical Acid Generating Potential (AGP) - Working Examples

This appendix includes working examples that demonstrate how the AGP of the Tui Mine tailings was estimated based on their sulphidic Fe & Cu content. Three examples are included for samples containing 1000 mg/kg pyritic Fe, 1000 mg/kg sulphidic Cu and a mixed sample containing 1000 mg/kg and 10 000 mg/kg of sulphidic Cu and Fe respectively. Assumptions made with respect to the use of this method are discussed in Chapter 4 (section 4.4).

AGP of Pyrite (FeS₂)

This method assumes that one mole of pyrite oxidises to form between 1.33 and 2.0 moles of H₂SO₄ (Bruynesteyn & Hackl, 1982). Therefore for every mole of pyrite oxidised between 1.33 and 1.0 mole of CaCO₃ is required to neutralise the acid produced.

General Data

pb (tailings)	≅ 1.3 Mg\m ³
Area (hectare)	= 10 000 m ²
Depth of sample	= 0.10 m

∴ Volume of tailings\ Ha = 0.1 * 10 000
= 1000 m³

∴ Mass of tailings\Ha ≅ 1000 * 1.3
≅ 1300 Mg/Ha

Molecular Masses

FeS₂ ≅ 55.847 + 2(32.06)
≅ 120 g

CaCO₃ ≅ 40.08 + 12.011 + 3(15.9994)
≅ 100.1 g

EXAMPLE 1 (Pyrite)

If tailings sample is analysed and found to contain 1000 mg/kg Fe as pyrite then the AGP of the sample can be estimated as follows:

Fe = 1000 mg/kg

∴ FeS₂ = (1000/55.847)*119.967(MW FeS₂)
= 2148 mg/kg

FeS₂ (%) = (2148 mg/kg /1000 000 mg/kg)*100/1
= 0.2148 %

$$\begin{aligned}
 \text{Mass (FeS}_2\text{/1000 Mg)} &= 1000 \text{ Mg} * 0.2148 \% \\
 &= 2.148 \text{ Mg} \\
 &= 2\,148\,000 \text{ g}
 \end{aligned}$$

$$\begin{aligned}
 \text{Moles (FeS}_2\text{/1000 Mg)} &= 2\,148\,000/119.967 \text{ (MW FeS}_2\text{)} \\
 &= 17.9 \text{ k moles FeS}_2
 \end{aligned}$$

∴ Moles of sulphuric acid potentially produced

$$\begin{aligned}
 \text{Lower limit} &= 17905 * 1.33 \\
 &= 23.8 \text{ k moles of H}_2\text{SO}_4
 \end{aligned}$$

$$\begin{aligned}
 \text{Upper limit} &= 17.9 * 2.0 \\
 &= 35.8 \text{ k moles of H}_2\text{SO}_4
 \end{aligned}$$

∴ Between 23.8 and 35.8 k moles of CaCO₃ will be required to neutralise the acid produced from 1000 Mg of tailings containing 0.2148 % pyrite (1000 mg/kg pyritic Fe)

Liming requirement in Mg CaCO₃/1000 Mg of material

$$\text{Mass of CaCO}_3 \text{ [Mg]} = (\text{moles of CaCO}_3 * \text{molecular weight of CaCO}_3) / 1000\,000$$

$$\begin{aligned}
 \text{Lower limit} &= (23813 * 100.1)/1000\,000 \\
 \text{AGP 1}^\circ &= 2.383 \text{ Mg CaCO}_3/1000 \text{ Mg} \\
 &= 2.4 \text{ Mg CaCO}_3/1000 \text{ Mg of tailings}
 \end{aligned}$$

$$\begin{aligned}
 \text{Lower limit} &= (35810 * 100.0892)/1000\,000 \\
 \text{AGP 2}^\circ &= 3.584 \text{ Mg CaCO}_3/1000 \text{ Mg} \\
 &= 3.6 \text{ Mg CaCO}_3/1000 \text{ Mg of tailings}
 \end{aligned}$$

EXAMPLE 2 (Chalcopyrite)

It is assumed that one mole of chalcopyrite (CuFeS₂) oxidises to form between 0.33 and 1.0 mole of H₂SO₄ (Bruynesteyn & Hackl, 1982). Therefore for every mole of chalcopyrite oxidised between 0.33 and 1.0 mole of CaCO₃ is required to neutralise the acid produced.

Atomic Masses

$$\begin{aligned}
 \text{Cu} &= 63.546 \text{ g} \\
 \text{Fe} &= 55.847 \text{ g} \\
 \text{S} &= 32.06 \text{ g} \\
 \text{CuFeS}_2 &= 183.513 \text{ g}
 \end{aligned}$$

$$\begin{aligned}
 \text{The amount of S associated with the Cu in chalcopyrite;} &= (1000/63.546) * 64.12 \\
 &= 1009 \text{ mg/kg}
 \end{aligned}$$

$$\begin{aligned}\text{The amount of Fe associated with the Cu in chalcopyrite;} &= (1000/63.546) * 55.847 \\ &= 879 \text{ mg/kg}\end{aligned}$$

If the tailings sample is analysed and found to contain 1000 mg/kg Cu all as chalcopyrite then the AGP of the sample can be estimated as follows:

$$\begin{aligned}\text{Cu} &= 1000 \text{ mg/kg} \\ \therefore \text{CuFeS}_2 &= (1000/63.546) * 183.513 \\ &= 2888 \text{ mg/kg} \\ \text{CuFeS}_2 (\%) &= (2888 \text{ mg/kg} / 1000 \text{ 000 mg/kg}) * 100/1 \\ &= 0.2888 \% \\ \text{Mass} &= 1000 \text{ Mg} * 0.2888 \% \\ (\text{CuFeS}_2/1000 \text{ Mg}) &= 2.888 \text{ Mg} \\ &= 2 \text{ 888 000 g} \\ \text{Moles} &= 2 \text{ 888 000} / 183.513 \text{ (MW CuFeS}_2\text{)} \\ (\text{CuFeS}_2/1000 \text{ Mg}) &= 15.7 \text{ k moles}\end{aligned}$$

$\therefore$ Moles of sulphuric acid potentially produced from the oxidation of 15.7 k moles of chalcopyrite;

$$\begin{aligned}\text{Lower limit} &= 15.7 * 0.33 \\ &= 5.2 \text{ k moles} \\ \text{Upper limit} &= 15.7 * 1.0 \\ &= 15.7 \text{ k moles}\end{aligned}$$

$\therefore$ Between 5.2 and 15.7 k moles of CaCO_3 will be required to neutralise the acid produced from 1000 Mg of tailings containing 0.2888% chalcopyrite (1000 mg/kg Cu)

Liming requirement in Mg CaCO_3 \1000 Mg of material

$$\begin{aligned}\text{Mass of CaCO}_3 [\text{Mg}] &= (\text{moles of CaCO}_3 * \text{molecular weight of CaCO}_3) / 1000 \text{ 000} \\ \text{Lower limit} &= (5246 * 100.0892) / 1000 \text{ 000} \\ \text{AGP 1}^\circ &= 0.5251 \text{ Mg CaCO}_3 \backslash 1000 \text{ Mg} \\ &= 0.5 \text{ Mg CaCO}_3 \backslash 1000 \text{ Mg}\end{aligned}$$

$$\begin{aligned}
 \text{Lower limit} &= (15737 * 100.0892)/1000\ 000 \\
 \text{AGP } 2^\circ &= 1.575 \text{ Mg CaCO}_3/1000 \text{ Mg} \\
 &= 1.6 \text{ Mg CaCO}_3/1000 \text{ Mg}
 \end{aligned}$$

EXAMPLE 3 (Mixed Sulphide Sample)

If tailings sample is analysed and found to contain 1000 mg/kg and 10 000 mg/kg sulphidic Cu and Fe respectively, the AGP of the sample can be estimated as follows:

Pyritic AGP

If Cu = 1000 mg/kg the amount of Fe associated with the Cu in chalcopyrite;

$$\begin{aligned}
 \text{Fe} &= (1000/63.546) * 55.847 \\
 &= 879 \text{ mg/kg}
 \end{aligned}$$

Therefore for every 1g of Cu analysed in solution 0.879 g of Fe will be associated with the Cu in the case of chalcopyrite, that is assuming all the Cu is derived from chalcopyrite.

The remaining Fe is assumed to be associated with pyrite.

$$\begin{aligned}
 \therefore \text{Fe (associated with FeS}_2\text{)} &= \text{Fe}_{(\text{total})} - \{(\text{Cu}_{(\text{total})}) * \text{Atomic weight ratio(Fe/Cu)}\} \\
 &= 10\ 000 - (1000 * 0.879) \\
 &= 9121 \text{ mg/kg} \\
 \text{AGP } 1^\circ (\text{FeS}_2) &= ([\text{Fe}]/1000) * 2.383 \\
 \text{(lower limit)} &= (9121/1000) * 2.383 \\
 &= 21.7 \text{ Mg CaCO}_3/ 1000 \text{ Mg of material}
 \end{aligned}$$

$$\begin{aligned}
 \text{AGP } 2^\circ (\text{FeS}_2) &= ([\text{Fe}]/1000) * 3.584 \\
 \text{(upper limit)} &= (9121/1000) * 3.584 \\
 &= 32.7 \text{ Mg CaCO}_3/ 1000 \text{ Mg of material}
 \end{aligned}$$

Chalcopyritic AGP

$$\begin{aligned}
 \text{AGP } 1^\circ (\text{CuFeS}_2) &= ([\text{Cu}]/1000) * 0.5251 \\
 \text{(lower limit)} &= (1000/1000) * 0.5251 \\
 &= 0.53 \text{ Mg CaCO}_3/ 1000 \text{ Mg of material}
 \end{aligned}$$

$$\begin{aligned}
 \text{AGP } 2^\circ (\text{CuFeS}_2) &= ([\text{Cu}]/1000) * 1.575 \\
 \text{(upper limit)} &= (1000/1000) * 1.575 \\
 &= 1.6 \text{ Mg CaCO}_3/ 1000 \text{ Mg of material}
 \end{aligned}$$

Total AGP

$$\begin{aligned}
 \text{Lower limit} &= \text{AGP } 1^\circ (\text{FeS}_2) + \text{AGP } 1^\circ (\text{CuFeS}_2) \\
 &= 21.7 + 0.53 \\
 &= 22.2 \text{ Mg CaCO}_3/1000 \text{ Mg material}
 \end{aligned}$$

$$\begin{aligned}
 \text{Upper limit} &= \text{AGP } 2^\circ (\text{FeS}_2) + \text{AGP } 2^\circ (\text{CuFeS}_2) \\
 &= 31.8 + 1.6 \\
 &= 34.3 \text{ Mg CaCO}_3/1000 \text{ Mg material}
 \end{aligned}$$

Stoichiometrically, the calcium carbonate equivalent of acid produced from a material containing, 10 000 mg/kg of Fe, and 1000 mg/kg of Cu in the form of FeS₂ and CuFeS₂ is between 22 and 35 Mg of CaCO₃ per 1000 Mg of material.

Appendix 4(I) Hydrogen Peroxide Oxidation AGP Method (NAG Method of Miller *et al.*, 1994)

Reactants

- (i) 15% Analytical Grade (unstabilised) H₂O₂

Method

- (i) Place 2.5 ± 0.1 g sample of pulverised * waste rock or tailings into a 500-mL conical glass beaker and add 250 mL of unstabilised 15% H₂O₂. Cover with watch-glasses and place in fume hood.
- (ii) Allow reaction to occur until either, (a) the sample boils then cools or (b) after at least 12 hours has elapsed.
- (iii) Heat sample on a hotplate at 100 °C until all effervescence ceases and the solution boils.
- (iv) After the solution has cooled measure the pH and the titratable acidity of the solution.
- (v) The titratable acidity of the solution is measured by titrating the solution to an endpoint of pH 7.0 using standardised 0.100 N NaOH. If the solution pH is < 2.5 use 0.500 N NaOH. If the sample gives a net acid generating potential equivalent value of > 25 Mg H₂SO₄/1000 Mg of material repeat the procedure using 1.0 g samples.

* The method provided did not state the grain-size to which the samples should be ground. Finkelman & Giffin (1986) recommended grinding the sample fine enough to remove the pyrite grain size effect; a grainsize of < 325 mesh (44 µm) was used. They state, however that the grain-size effect can yield useful information on the mean or effective pyrite grain-size, a useful parameter for spoil handling strategies as sample reactivity is strongly dependent on the size factor. However for the purposes of this study, the samples were ground to < 150 µm with a tungsten-carbide ring grinder. Unground samples were also run.

Appendix 4(J)**Neutralising Potential Method**
(Adapted from Sobek *et al.*, 1978)**Method**

- (i) Add 50 mL of 0.1M HCl to a 2.0 g tailings sample ($< 150 \mu\text{m}$).
- (ii) Heat the solution at near boiling, stirring occasionally until CO_2 evolution ceases.
- (iii) Make the solutions up to 125 mL with distilled water.
- (iv) Boil samples for 1 minute.
- (v) Allow samples to cool to room temperature.
- (vi) Titrate samples with standard 0.1M NaOH solution to pH 7.0 using a pH meter as per the titration method outlined below.
- (vii) Repeat titration on duplicate sample reacting with distilled water.

Titration Method

- (i) A few drops of methyl red indicator were placed in the cooled solutions prior to titration to indicate when the solution was approaching pH 7.0. (Methyl red changes colour from red to yellow in the pH range of 4.8 to 6.0)
- (ii) The samples were gently agitated during the titration by a flea and magnetic stirrer to mix the solution as the NaOH was added by burette. A pH meter was used to take the solution to the endpoint pH 7.0, after solution colour change occurred.

Calculation of CaCO_3 equivalent from NaOH consumption

The calcium carbonate equivalent of a material can then be calculated stoichiometrically based on its consumption of HCl. Firstly the moles of 0.10M HCl added to the sample are calculated using Equation 1.

[Equation 1]

$$\begin{aligned} \text{Moles HCl added} &= \text{initial volume HCl added [mL]} \times \text{concentration [M]} / 1000 \text{ mL} \\ &= A \end{aligned}$$

Secondly the number of moles of NaOH required to neutralise the acid remaining in solution after the reaction are calculated using Equation 2.

[Equation 2]

$$\begin{aligned} \text{Moles NaOH required} &= \text{volume NaOH added [mL]} \times \text{concentration [M]} / 1000 \text{ mL} \\ &= B \end{aligned}$$

Since 1 mole of NaOH reacts with 1 mole of HCl, it is possible to calculate the number of moles of HCl consumed by the reaction of the material with the acid by Equation 3.

$$\text{[Equation 3] Moles of HCl consumed by sample} = A - B$$



Based on Equation 4 it is seen that 1.0 mole of CaCO_3 neutralises 2.0 moles of HCl . Therefore the number of moles of CaCO_3 required to neutralise the moles of acid consumed by the reaction is shown in Equation 5.

[Equation 5] Moles of $\text{CaCO}_3 = A - B / 2$

Since one mole of $\text{CaCO}_3 = 100 \text{ g}$, the amount of CaCO_3 [$\text{g CaCO}_3/\text{g material}$] required to neutralise the acidity produced by a given mass of material equals;

[Equation 6] Calcium Carbonate equivalent = moles $\text{CaCO}_3 \times 100\text{g} / \text{sample mass} [\text{g}]$

Conversion to $\text{Mg CaCO}_3/1000 \text{ Mg material}$ is made by multiplying the answer by 1000. The above calculations do not take into consideration the inherent acidity of a sample. Failure to take the materials free-acidity into account may result in the underestimation of the materials neutralising capacity, because a small amount of NaOH will be required to neutralise the free acidity of the material if present. The sample's inherent acidity can be calculated by running a duplicate sample treated with distilled water rather than acid and then titrated in the same fashion (Equation 7).

[Equation 7]

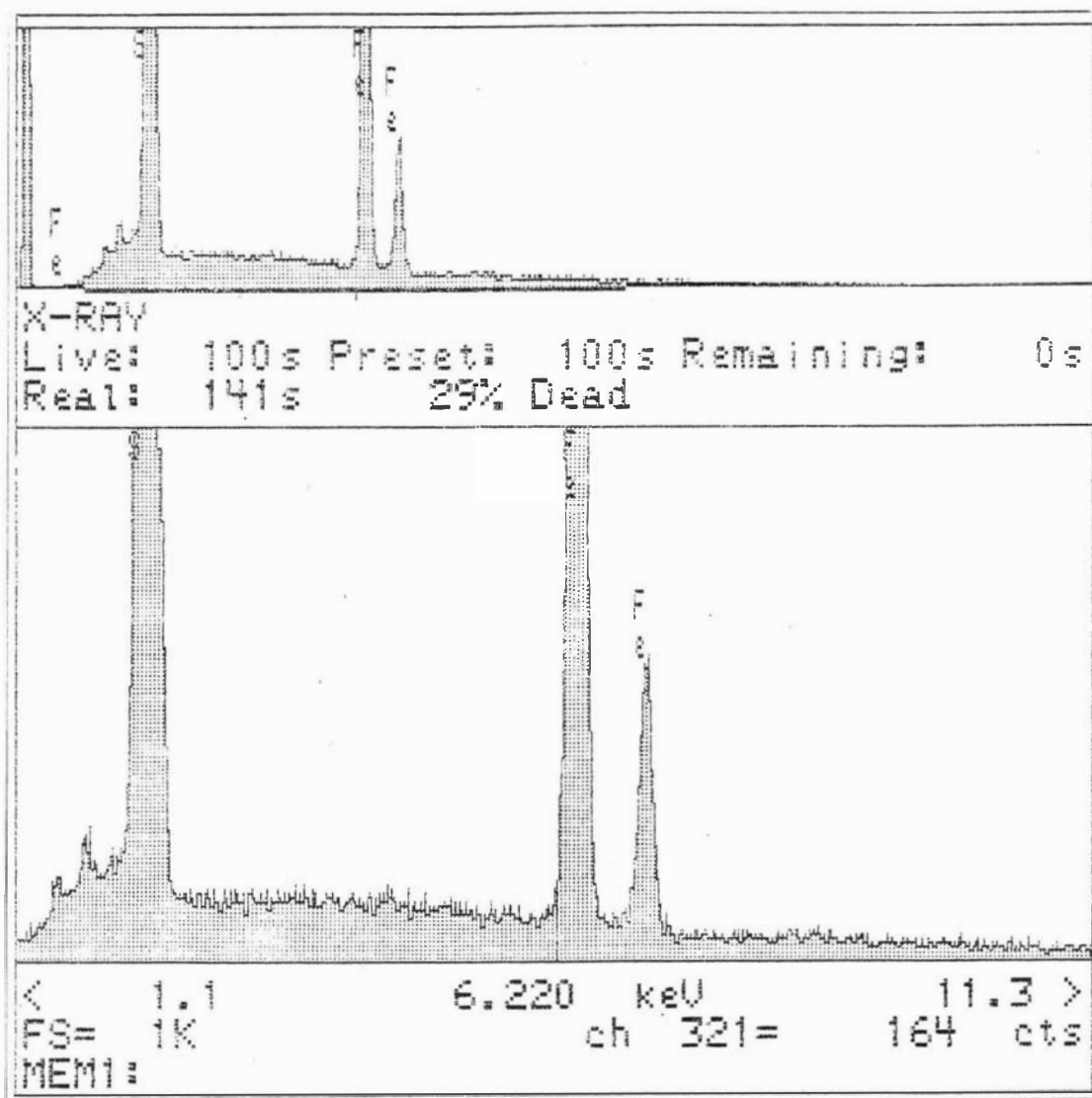
$$\begin{aligned} \text{Moles NaOH consumed} &= \text{volume NaOH added [mL]} \times \text{concentration [M]} / 1000 \text{ mL} \\ \text{by samples free-acidity} &= C \end{aligned}$$

These equations can be combined to enable allow rapid calculation of the theoretical NP of a sample as follows;

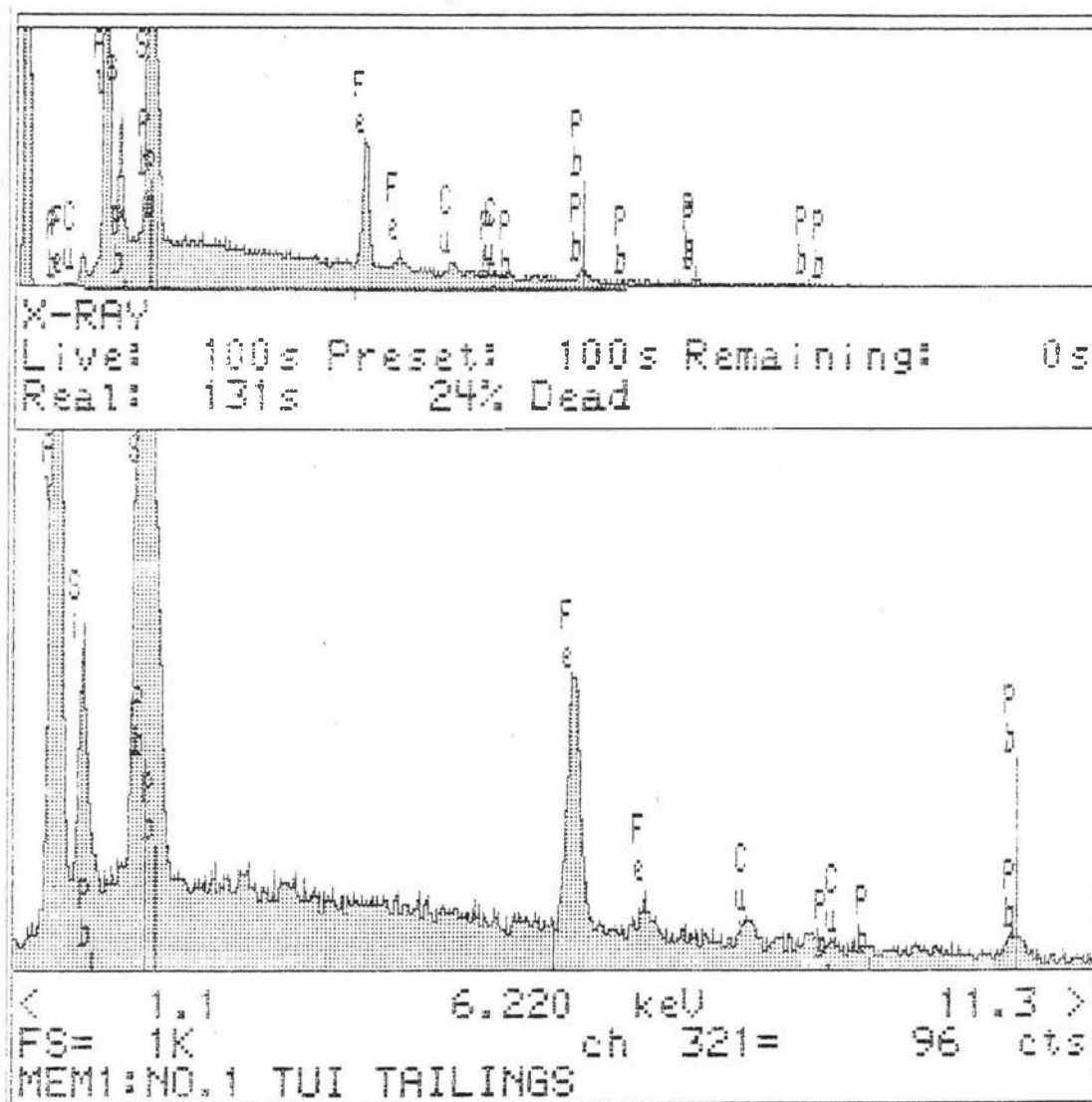
$$\text{Neutralising potential} = (A - B) + C \times 1 \times 10^5 / 2 \times \text{sample mass [g]}$$

[$\text{Mg CaCO}_3 / 1000 \text{ Mg of material}$]

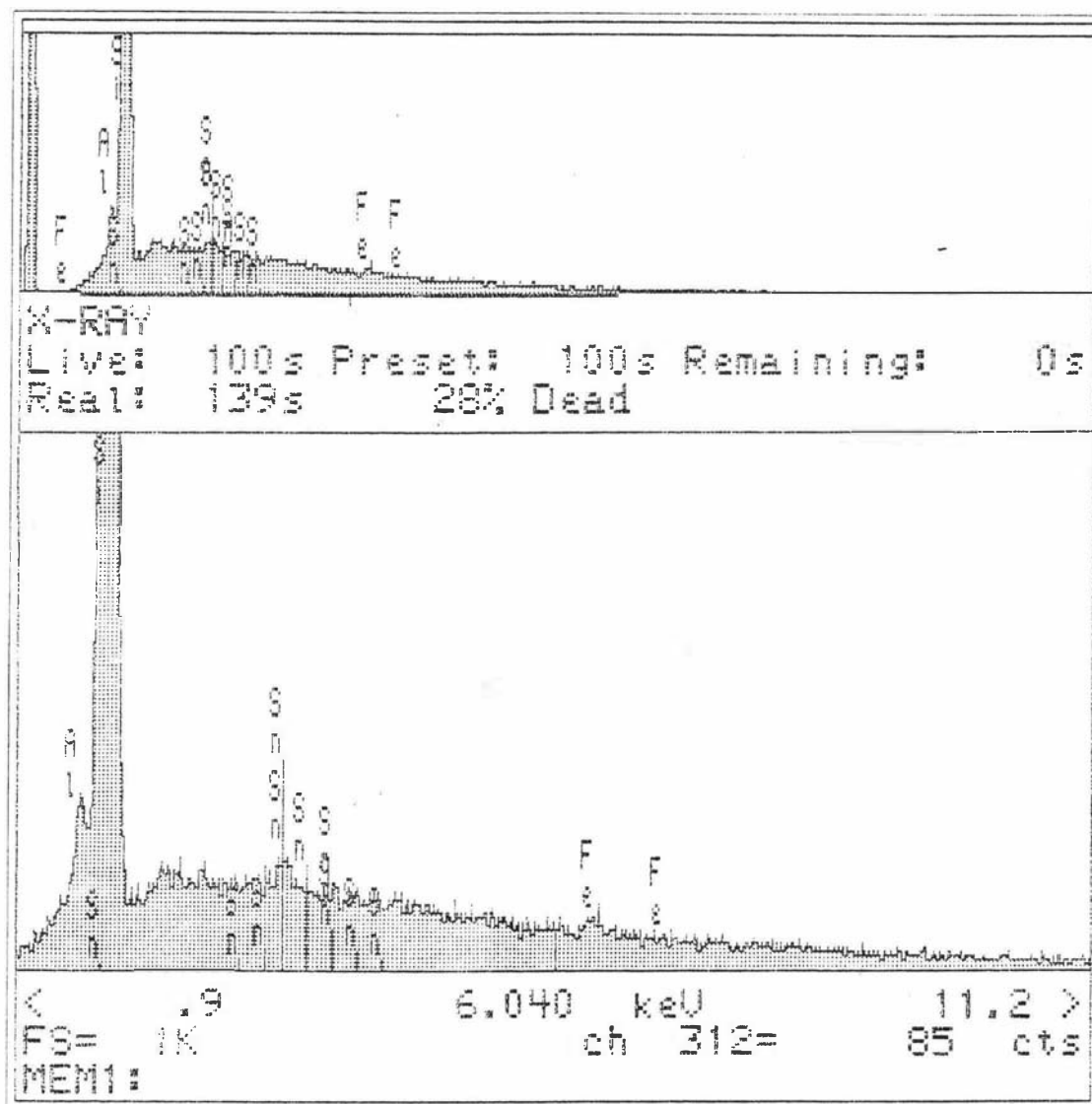
Where **A** = moles of acid originally added to the sample, **B** = moles of NaOH required to neutralise excess acid and **C** = moles of NaOH neutralised by sample acidity.



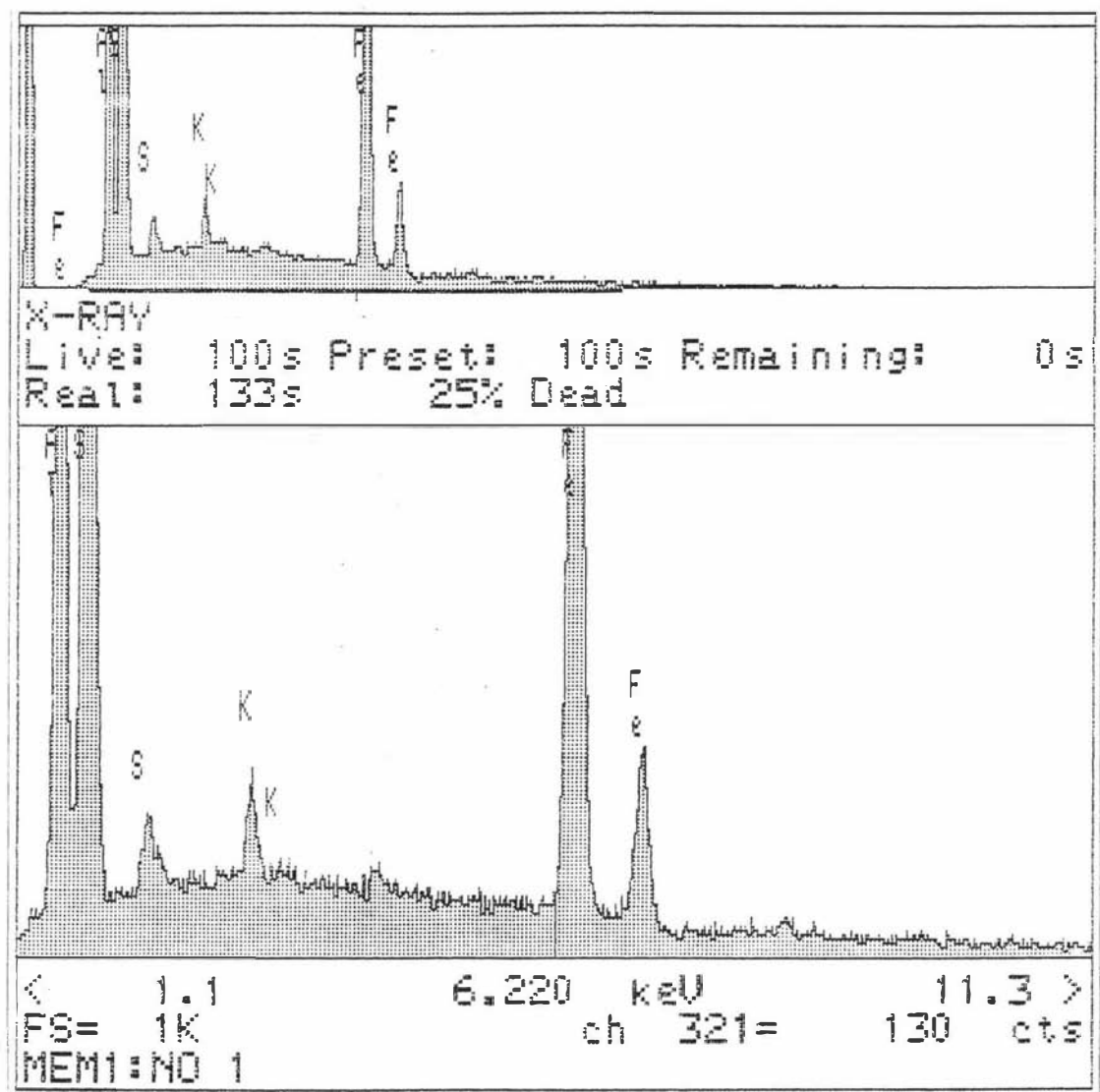
Appendix 5(A) EDS spectrum for a pyrite cube such as those visible in Plate 5.2. The 3 major peaks are associated with the S and Fe constituents of iron pyrite. Very little 'contamination' is evident.



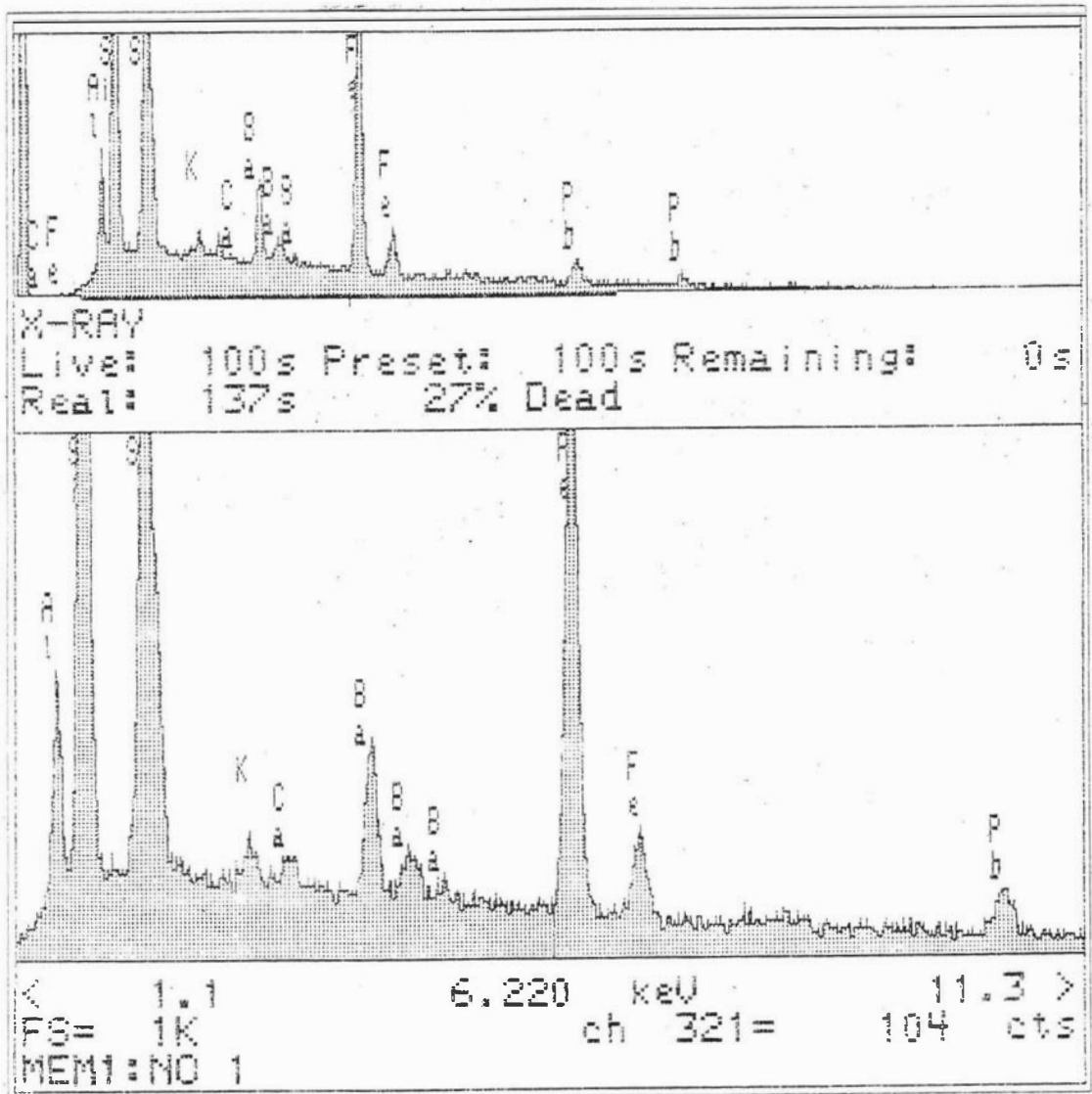
Appendix 5(B) EDS spectrum for an 'aggregate grain' such as that seen in Plate 5.6. The major peaks are associated with Al, Fe, Si, S and possibly Pb. Trace quantities of Cu were also identified in the sample.



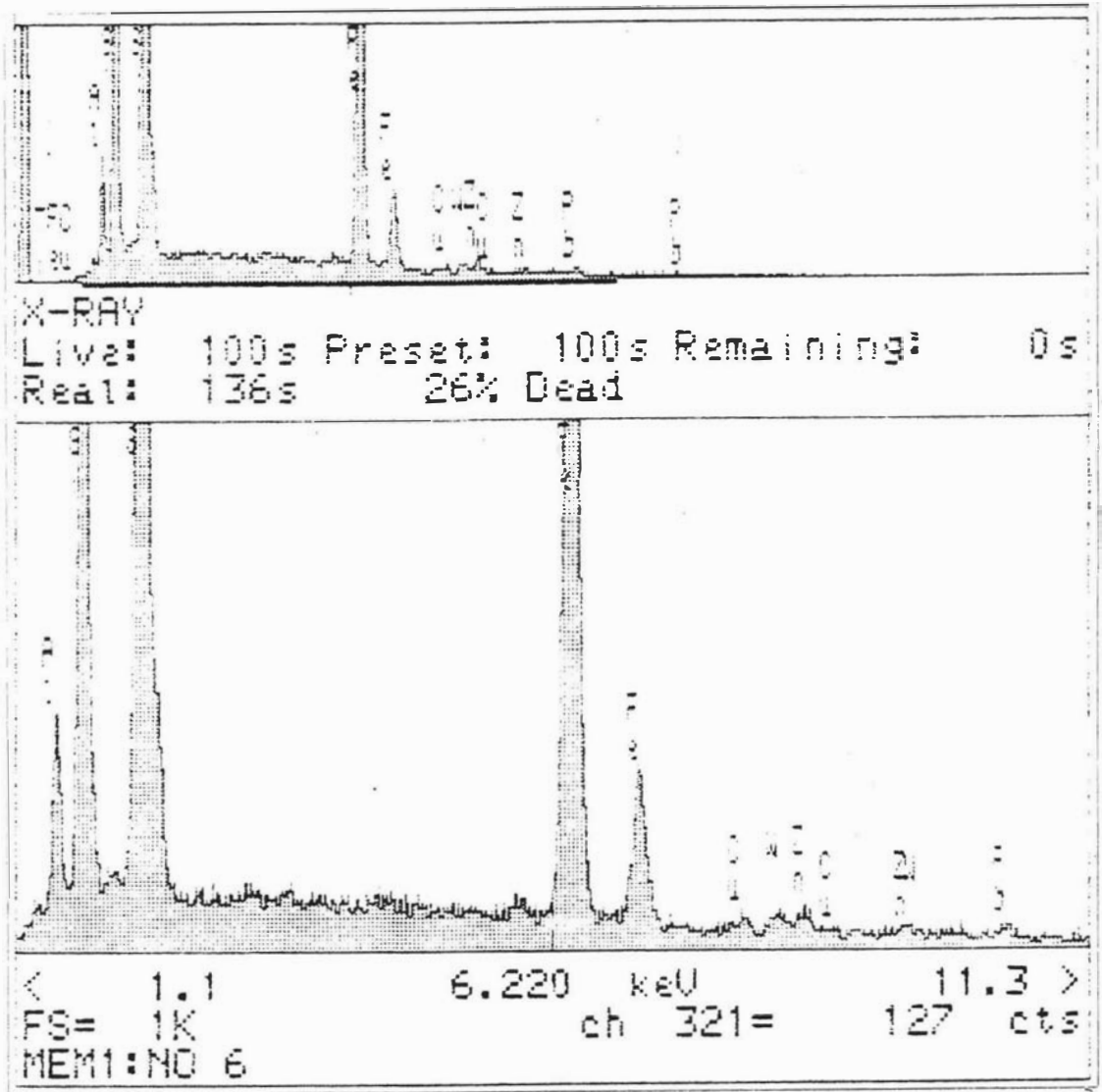
Appendix 5(C) EDS spectrum for the quartz grain shown in Plate 9. The major peak is that of Si, however, minor quantities of Al, Fe and Sn were also detected in the sample.



Appendix 5(D) This EDS spectrum identifies the presence of K in the tailings probably in the form of mica. The occurrence of a large Fe peak and relatively small S peak indicate that the Fe is probably in the form of oxides or aluminosilicate clays as opposed to sulphides.



Appendix 5(E) Low magnification (180 x) EDS spectrum for the 0-100 mm tailings sample. A significant amount of Ba was identified in 3 EDS taken in the surface horizon. Pb concentrations also tended to be higher relative to the 500-600 mm sample.



Appendix 5(F) Low magnification (180 x) EDS spectrum for the 500-600 mm tailings sample. The 3 EDS samples showed little or no Ba and unlike the surface sample Cu, W and Zn were detected in all 3 low magnification EDS analyses at this depth.

Appendix 6(A)**Liming Requirement Based on pH Buffering**
(Massey University Soils Dept. Standard Method)

1. Duplicate 20g tailing samples were weighed into a set of six 120-mL plastic beakers.
2. The following volumes of water and 0.2M NaOH were added.

Beaker #	Volume of Distilled H ₂ O Added [mL per beaker]	Volume of Distilled NaOH Added [mL per beaker]
1	10	0
2	8	2
3	6	4
4	4	6
5	2	8
6	0	10

4. The samples were stirred, covered with Parafilm, and left to incubate at 25°C for 48 hours.
5. After the incubation period 40 mL of distilled water was added to each of the samples to obtain a 1:2.5 tailings-to-solution ratio.
6. The solution was stirred and allowed to settle for approximately ½ an hour, and then the pH of the solutions was measured.
7. A graph of pH against *mmol* of NaOH added was plotted.
8. From the individual graphs for each sample the theoretical quantity of lime required to increase the pH of the tailings to 6.0 was calculated.
9. Graphs were plotted using Grapher for Windows version 1.20. A linear best fit curve was plotted to obtain the pH buffering curve data.

Appendix 6(B) Acid Generation Estimates Based on Hydrogen Ion Liberation

This appendix includes a working example of a method used to compare the relative reactivity of incubated Tui tailings samples in terms of their ability to generate acidity. The method involved the use of pH values to estimate the quantity of hydrogen ion (H^+) liberated over the course of a 1½ year lime incubation experiment. The estimated acidity produced by the tailings samples was converted into units of calcium carbonate equivalence [Mg $CaCO_3$ /1000 Mg tailings].

General Data

- The example outlined below assumes that the hypothetical tailings sample had an initial pH (pH_i) of 5.0 and a final pH (pH_f) of 2.0 at the end of the incubation period.
- pH measurements were made using a 10g to 25 mL ratio of tailings to distilled water as per the method outlined in Chapter 4 (section 4.1.1.1)
- Molecular weight of calcium carbonate ($CaCO_3$) $\cong$ 100.1 g
- The concentration of $H^+ = 10^{-pH}$ [moles/L]

Working

$$\begin{aligned} pH_i &= 5.0 \\ [H^+]_i &= 5.0 \times 10^{-5} \text{ moles/litre/10g of tailings} \end{aligned}$$

$$\begin{aligned} pH_f &= 2.0 \\ [H^+]_f &= 2.0 \times 10^{-2} \text{ moles/litre/10g of tailings} \end{aligned}$$

$$\begin{aligned} \Delta [H^+] &= 2.0 \times 10^{-2} - 5.0 \times 10^{-5} \\ &= 1.995 \times 10^{-2} \text{ moles/litre/10g of tailings} \end{aligned}$$

$\therefore$ Mole of H^+ per kg of tailings

$$\begin{aligned} &= \frac{1.995 \times 10^{-2} \times 25 \text{ mL} \times 1000 \text{ g}}{1000 \text{ mL} \times 10 \text{ g}} \\ &\cong 4.988 \times 10^{-2} \text{ moles/kg tailings} \\ &\cong 49.88 \text{ moles/Mg of tailings} \\ &\cong 49880 \text{ moles/1000 Mg of tailings} \end{aligned}$$

As discussed in Chapter 4 the dissociation of 1.0 mole of $CaCO_3$ in water effectively results in the formation of products that can neutralise 2.0 moles of H^+ . Therefore 100.1g of $CaCO_3$ will neutralise 2.0 moles of H^+ . The acid produced by from the tailings in units of Mg $CaCO_3$ /1000 Mg tailings is thus calculated as follows;

$$\begin{aligned} &\cong \frac{100.1 \text{ g} \times 49880 \text{ moles}}{2 \text{ moles} \times 1000 \times 1000} \\ &\cong 2.5 \text{ Mg } CaCO_3/1000 \text{ Mg tailings} \end{aligned}$$

Appendix 7(A) Seed Germination Trial Results

Metal	<i>A. capillaris</i> (Egmont)	<i>A. capillaris</i> (Goginan)	<i>A. capillaris</i> (Parys Mountain)	<i>F. rubra</i> (Merlin)	<i>F. rubra</i> (Lobi)
Cu					
[µg/L]					
0	***	**	***	***	***
5	***	**	***	***	***
10	**	*	***	***	**
20	*	0	**	***	0
50	0	0	0	***	0
100	0	0	0	0	0
Pb					
[µg/L]					
0	***	**	***	***	***
5	***	**	***	***	***
10	***	**	***	***	***
20	***	**	***	***	***
50	***	**	***	***	***
100	***	*	***	***	***
Zn					
[µg/L]					
0	***	**	***	***	***
5	***	**	***	***	***
10	***	**	***	***	***
20	***	**	***	***	***
50	***	**	***	***	***
100	***	**	***	***	***

(*** = high germination, ** = medium germination , * = low germination, 0 = nil germination)

Appendix 7(B)

Trial Two: Organic Matter Rate Calculations

Desired Organic carbon content = 4 % .
O. carbon content of sludge = 23.6 %
Bulk density of tailings = 1.30 Mg/m³
Assume incorporation depth = 0.2 m
Therefore Mg tailings/ha = 10, 000 x 0.2 x 1.3 = 2,600

∴ Sludge Application rate = (2,600 x 0.04)/0.236 ≅ 440 Mg/ha

Sludge Rate [Mg/ha]	0	110	220	440
Dry Sludge per Bag [g]	0	42.3	84.5	169
Moist Sludge per Bag [g]	0	78	156	312
Total Dry Weight [g]	1000	1042.3	1084.5	1169
Total Water Content	6.8 %	9.4 %	11.8 %	15.6 %

Please Note: Raw analytical data pertaining to this thesis is to be held on CD-ROM by the Department of Soil Science at Massey University, Private Bag 11222, Palmerston North, New Zealand.