

# REVEGETATION AND PHYTOREMEDIATION OF TAILINGS FROM A LEAD/ZINC MINE AND LAND DISPOSAL OF TWO MANGANESE-RICH WASTES

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BSc Hons (UNP), MSc *cum laude* (UNP)

Submitted in fulfilment of the academic  
requirements for the degree of

Doctor of Philosophy

in the Discipline of Soil Science,  
School of Environmental Sciences,  
University of KwaZulu-Natal  
Pietermaritzburg

2007

## ABSTRACT

The original aims of this project were to investigate the potential for phytoremediation, with emphasis on metal accumulation, of three contrasting industrial processing wastes. These were tailings material (PT) from the decommissioned Pering Pb/Zn Mine (Reivilo, North West Province, South Africa (SA)), smelter slag (SS) from the Samancor Mn-smelter (Meyerton, Gauteng, SA) and electro-winning waste (EW) from MMC (Nelspruit, Mpumalanga, SA). It became evident, however, early in the project, that the use of metal hyperaccumulating plants was not a viable technology for these wastes. The project objectives were thus adapted to investigate alternative remedial technologies. The use of endemic and adapted grass species was investigated to revegetate the PT. In addition, chemically-enhanced phytoremediation was investigated to induce metal hyperaccumulation by grasses grown in the PT (Part 1). Revegetation of the SS and EW were not considered feasible, thus land disposal of these two Mn-rich processing wastes was investigated (Part 2).

### Part 1 - Revegetation of tailings from Pering Mine

The PT was found to be alkaline ( $\text{pH} > 8.0$ ), and consisted mainly of finely crushed dolomite. It was generally nutrient poor with high amounts of readily extractable Zn. It also had a very high P-sorption capacity. Seven grass species (*Andropogon eucomus* Nees; *Cenchrus ciliaris* L.; *Cymbopogon plurinodis* Stapf ex Burt Davy; *Digitaria eriantha* Steud; *Eragrostis superba* Peyr; *Eragrostis tef* (Zucc.) Trotter and *Fingeruthia africana* Lehm) were grown in PT treated with different rates of inorganic fertiliser under glasshouse conditions. The fertiliser was applied at rates equivalent to 100 kg N, 150 kg P and 100 kg K ha<sup>-1</sup> (full), half the full rate (half) and no fertiliser (0). Seed of *C. ciliaris*, *C. plurinodis*, *D. eriantha*, *E. superba* and *F. africana* were collected from Pering Mine. Seed of *A. eucomus* was collected from the tailings dam of an abandoned chrysotile asbestos mine. These were germinated in seedling trays and replanted into the pots. A commercial variety of *E. tef* was tested, but due to poor survival this species was subsequently excluded. The foliage and root biomass of the grasses and concentrations of Ca, Cu, Fe, K, Mg, Mn, Pb and Zn in the foliage were determined.

The yield of all the grasses increased with an increase in fertiliser rate, with a significant species by fertiliser interaction ( $p = 0.002$ ). The highest yield was measured for *C. ciliaris*, followed by *D. eriantha* (4.02 and 3.43 g pot<sup>-1</sup>, respectively), at the full fertiliser application rate. *Cymbopogon plurinodis* was the third highest yielding species, while the yields of *E. superba* and *F. africana* were similar. There were positive linear correlations between foliage yield and fertiliser application rate for all grasses. The root biomass of the grasses also increased with an increase in fertiliser application rate. The interaction between grass species and fertiliser level had a non-significant ( $p = 0.085$ ) effect on the yield of grasses, though there were significant individual effects of species ( $p < 0.001$ ) and fertiliser ( $p < 0.001$ ). *Digitaria eriantha* had the highest root biomass at each fertiliser application rate, followed by *C. plurinodis* and *C. ciliaris*. Similarly to foliage yield, there were positive linear correlations between root biomass and fertiliser application level. Positive, linear correlations were found between foliage yield and root biomass, though the strength of these varied. The weakest correlation was found for *D. eriantha* ( $R^2 = 0.42$ ) but this was attributed to a moderately high variance in foliage yield and roots becoming pot-bound. Generally, nutrient concentrations were within adequacy ranges reported in the literature, except for P concentrations. This was attributed to the high P-sorption capacity of the PT. Zinc concentrations were higher than the recommended range for grasses, and also increased with an increase in fertiliser application rate. This was attributed to the high available Zn concentrations in the PT and improved growth of the grasses at higher fertiliser application rates. It was recommended that *C. ciliaris* and *D. eriantha* be used for revegetation due to high biomass production and that *E. superba* be used because of rapid growth rate and high self-propagation potential. Both *C. plurinodis* and *F. africana* can also be used but are slower to establish, while *A. eucomus* was not a suitable species for revegetation of the PT. Inorganic fertiliser improved the growth of all these species and is recommended for the initial establishment of the grasses.

An experiment was conducted to investigate the potential of inducing metal hyperaccumulation in three grass species (*C. ciliaris*, *D. eriantha* and *E. superba*) grown in the PT. Grasses were grown in fertilised tailings for six weeks, then either ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA) was added to the pots at rates of 0, 0.25, 0.5, 1 and 2 g kg<sup>-1</sup>. Grasses were allowed to grow for an additional week before harvesting. The concentrations of Cu, Pb and Zn were determined in the foliage. The interactive effect of species and chelating agent on the

uptake of Cu was marginally significant ( $p = 0.042$ ) and non-significant for Pb and Zn ( $p = 0.14$  and  $0.73$ , respectively). While the addition of the chelating agents resulted in an increase in Pb uptake by the grasses, it did not induce metal hyperaccumulation in the grasses. This was attributed to the ineffectiveness of the chelating agents in the PT in the presence of competing base cations (mainly Ca). The use of this technology was not recommended.

## **Part 2 - Land disposal of Mn-rich processing wastes**

Chemical characterisation of the SS showed that it was an alkaline ( $\text{pH} > 9.5$ ), Mn-rich silicate (glaucobroite), that generally had low amounts of soluble and readily extractable metals. Acidic extractants removed high amounts of Mn, Ca and Mg, attributed to the dissolution of the silicate mineral. The EW was highly saline (saturated paste  $\text{EC} = 6\,780\text{ mS m}^{-1}$ ) with a near-neutral pH. It had high amounts of soluble Mn,  $\text{NH}_4^+$ , S, Mg, Ca and Co. The primary minerals were magnetite, jacobsonite ( $\text{MnFe}_2\text{O}_4$ ) and gypsum.

The effect of SS and EW on selected chemical properties of six soils was investigated by means of an incubation experiment, and their effect on the yield and element uptake by ryegrass was investigated in selected soils under glasshouse conditions. Five A-horizons (Bonheim (Bo), Hutton (Hu), Inanda (Ia), Shortlands (Sd) and Valsrivier (Va)) and an E-horizon (Longlands (Lo)) were treated with SS at rates of 30, 60, 120, 240 and  $480\text{ g kg}^{-1}$  and EW at rates of 20, 40, 80, 160 and  $320\text{ g kg}^{-1}$ . Soils were incubated at field capacity at  $24\text{ }^\circ\text{C}$  and sampled periodically over 252 days. The soil pH, both immediately and over time, increased, while exchangeable acidity decreased after the addition of SS to the soils. The pH at the high rates of SS tended to be very high (about 8). The electrical conductivity (EC) of the soils also increased with an increase in SS application rates and over time. The most marked changes tended to occur in the more acidic soils (e.g. Ia). In the soils treated with EW, there was generally an increase in the pH of the acid soils (e.g. Ia) while in the more alkaline soils the pH tended to decrease (e.g. Va), immediately after waste application. There was a general decrease in pH over time, with a concurrent increase in exchangeable acidity, due to nitrification processes. The EC of all the soils increased sharply with an increase in EW application rate, attributed to the very saline nature of the EW.



Water-soluble Mn concentrations in the soils treated with SS tended to be below measurable limits, except in the acid Ia. Iron concentrations decreased with an increase in SS application rate and over time for all soils. The water-soluble concentrations of Mn, Ca, Mg and S increased sharply with an increase in EW application rate in all soils. There was also a general increase in Mn concentrations over time. Iron concentrations tended to be low in the EW-treated soils, while Co concentrations increased as EW application rate increased.

Exchangeable (EX, 0.05 M  $\text{CaCl}_2$ -extractable) concentrations of Fe, Co, Cu, Zn and Ni were low in the SS-treated soils. The concentrations of EX-Mn tended to increase with an increase in SS application rate in the Ia soil, but generally decreased in the other soils. There was also a decrease over time, attributed to the high pH leading to immobilisation of Mn. The EX-metal concentrations of the EW-treated soils were generally low, except for Mn. The concentrations of EX-Mn increased sharply as EW application rate increased. The contribution of EX-Mn was calculated to range from 209 to 3 340 mg Mn for EW rates of 20 to 320 g  $\text{kg}^{-1}$ , respectively. In the Lo soil the expected amount of Mn was extracted at the different EW application rates. In the other soils the EX-Mn concentrations were typically higher than expected. This was attributed primarily to the dissolution of Mn from the EW due to the interaction between soil organic matter and the EW. There was generally an increase in EX-Mn concentrations over time, attributed to the decrease in pH of the soils treated with EW.

The above-ground biomass production of ryegrass grown in Lo and Hu soils treated with SS increased at low application rates, but decreased again at the highest rates. The reduction in yield was attributed to an increase in soil pH leading to trace nutrient deficiencies. At the lower SS application rates, nutrient concentrations of the ryegrass tended to be within typical adequate ranges reported in the literature. Of concern was the elevated Mn concentration in the ryegrass foliage, though no toxicity symptoms were seen. This was attributed to the dissolution of the silicate mineral due to soil acidification processes and the possible ameliorating effect of high Ca and Si concentrations on Mn toxicity.

The growth of ryegrass was generally poor in the Hu soil treated with EW and it did not survive beyond germination in the Lo soil treated with EW. In the Hu soil plants grew well

in the 20 and 40 g kg<sup>-1</sup> EW treatments, but died at the higher rates. In both cases mortality was thought to be due to the high salinity that resulted in toxicity and osmotic stress in the newly germinated seedlings. The improved growth at the lower rates of EW, in the Hu soil, was attributed mainly to increased N availability. The concentrations of Mn in the foliage were elevated in the soils treated with EW.

A pot experiment was conducted to test the effect of applying either humic acid (HA) or compost (at a rate of 20 g kg<sup>-1</sup>) with lime (at rates of 0, 5 and 10 Mg ha<sup>-1</sup>) on the growth and nutrient uptake of ryegrass grown in the Hu soil treated with EW at rates of 0, 10, 20 and 40 g kg<sup>-1</sup>. A basal P-fertiliser was also applied in this experiment. The highest yields were measured in the treatments receiving either HA or compost at the highest application rate of EW. The addition of lime did not improve the yield of the HA treatments, but did in the compost treatments. Generally, nutrient concentrations were adequate. The Mn concentrations were markedly lower than expected, and this was attributed to the formation of insoluble Mn-P compounds due to the addition of fertiliser. The effect of either HA or compost on Mn concentrations was not marked, but lime reduced Mn uptake. A leaching column experiment showed that, generally, the Mn was not readily leached through a simulated soil profile, though the addition of compost may enhance mobility. There was also evidence to indicate an increase in salinity and that Co concentrations of the leachate may be a problem.


These data suggest that soil organic matter may be a very important factor in determining the release of Mn from the wastes, notably the EW. The land disposal of the SS and EW was not recommended at the rates investigated here, as both showed the potential for Mn accumulation in above-ground foliage, even at low application rates, while high application rates negatively impacted on plant growth. It appears that P-compounds may be beneficial in reducing Mn availability in the EW, but further testing is required.

## DECLARATION

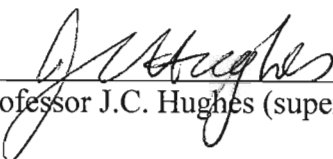
The experimental work described in this thesis was carried out in the School of Environmental Sciences, University of KwaZulu-Natal, Pietermaritzburg, from January 2004 to January 2007, under the supervision of Professor J.C. Hughes.

These studies represent original work by the author and have not been submitted in any form for any degree or diploma to any other University. Where use has been made of the work of others it is duly acknowledged in the text.

Signed:

  
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16 July 2007  
Date

  
\_\_\_\_\_  
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17/7/07  
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## ACKNOWLEDGEMENTS

I would like to thank the following people and organisations for their assistance:

Mr H.C. Bester for giving me the opportunity to conduct this research (with a salary) and the advice (regarding both the research and life in general) I received along the way, I have thoroughly appreciated your enlightened look on life;

Professor J.C. Hughes for your ever-useful advice and remarkable patience throughout the course of this work (and long before), you are a great mentor and an exceptional academic inspiration;

BHP-Billiton for providing the wastes and the funding to conduct the research;

THRIP for additional funding on the project;

Mrs. R. Muhlbauer, Ms. S. Raja and Dr. D. Dew and all the other staff of BHP-Billiton JTC that were involved in this work;

The staff of Pering Mine, Samancor and MMC that assisted us during our visits to these sites;

Ms. D Hlabisa, Mr. E. Abib, Mr. V. Dorasamy, Mr. J.M. Buthelezi, Mr. D. Elephant, Ms. N. Mthwane, Mr. J.S. Buthelezi and Mrs. T. Nala for all their help with various aspects of the work;

Dr. D. Smith for assistance in the laboratory, advice (with so many things) and being a friend;

Dr. C. Southway (School of Chemistry) for use of the ICP and Mr L. de Klerk (CERU) for use of the glasshouse;

The Discipline of Geology for XRF analyses, the Centre for Electron Microscopy, in particular Mrs B. White, for help with the electron microscope, the Mechanical Instruments Workshop for constructing equipment, Mr. P. Forder for your glassblowing skills and Mr. J. Naiken for use of the Grassland Science vehicles;

The staff of the Soil Fertility and Analytical Services Division (KwaZulu-Natal Department of Agriculture, Cedara), in particular, Mr. G. Thibaud, for analyses and advice;

Zylem Pty. (Ltd.) for supplying the humic and fulvic acids;

Ms. D. Rietz, Mr. T. Vergunst and Mrs S. Govender for their general helpfulness, advice and friendship;

To anyone or any organisation I may have omitted, I promise it was not intentional;

To my mother, Hester, stepfather, Nic, and brother, Julian you have supported me in more ways than I can express, I am most appreciative;

And last but certainly not least, my loving wife, Catherine. You are my world and without you I would be lost. You have been there for me every step of the way, I appreciate everything you do for me and I am eternally grateful.

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## LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrophotometry
AEE	Acceptable environmental exposure
AHHE	Acceptable human health exposure
AMBIC	0.25 M ammonium bicarbonate (pH 8.3)
AMOX	Amorphous oxide bound (acid oxalate (pH 3) extractable)
ANOVA	Analysis of variance
BCF	Bioconcentration factor
bd	below detection
Bo	Bonheim soil form
CCE	Calcium carbonate equivalence (%)
CDTA	1,2 cyclohexylenedinitrilotetraacetic acid
CEC	Cation exchange capacity ( $\text{cmol}_c \text{ kg}^{-1}$ )
DTPA	Diethylenetriaminepentaacetic acid
DWAF	Department of Water Affairs and Forestry
EC	Electrical conductivity ( $\text{mS m}^{-1}$ )
ECA	Environmental Conservation Act
EDTA	Ethylenediaminetetraacetic acid
EDX	Electron dispersive x-ray
EEC	Estimated environmental concentration
EMP	Environmental management plan
ESEM	Environmental scanning electron microscope
EW	Electro-winning waste from the MMC Mn-electro-winning plant
EX	Exchangeable (0.05 M $\text{CaCl}_2$ extractable)
FA	Fulvic acid
HA	Humic acid
HEDTA	Hydroxyethylentriaminetriacetic acid
Hu	Hutton soil form
Ia	Inanda soil form
IB	Inorganically bound (2.5% acetic acid extractable)
ICP	Inductively coupled plasma emission spectrometry

Lo	Longlands soil form
LSD	Least squares differences
MER	Metal extraction ratio
MMC	Manganese Metal Company
MRPDA	Mineral Resources and Petroleum Development Act
na	data not available
nd	not determined
NEMA	National Environmental Management Act
NWA	National Water Act
OB	Organically bound (0.1 M $K_4P_2O_7$ extractable)
OC	Organic carbon
OM	Organic matter
PT	Tailings from Pering Mine
SA	South Africa
SAR	Sodium absorption ratio
Sd	Shortlands soil form
SE	Standard error
SeSl	Sewage sludge
SP	Saturation percentage (%)
SS	Slag from the Samancor Mn-Smelter
TCLP	Toxicity characteristic leaching procedure
UV-vis	UV-visible spectrophotometer
Va	Valsrivier soil form
XRD	X-ray diffraction analysis
XRF	X-ray fluorescence analysis

# CHAPTER 1

## PREAMBLE

### 1.1 Introduction

Hazardous waste generation is becoming a serious threat to environmental resources and much effort is now invested to find possible solutions to the problem. While the production of waste is an almost inevitable result of industrial activity, steps can be taken to reduce the amounts of waste generated. The South African Department of Water Affairs and Forestry (DWAF, 2005) promotes the philosophy of the three R's namely reduce, reuse and recycle. However, the complete elimination of waste is never likely to occur. Thus there will always be a need for alternative disposal options. In some instances, like the waste generated from mining (tailings and spoils), the best method to stabilise the waste is by revegetation technology. However, this is not always possible. Often, when industry is involved in processing raw materials, the wastes are not suitable for direct revegetation due to physical and chemical constraints, as well as logistical limitations. In these instances alternative waste disposal treatment is required. In a few cases wastes can be beneficially used by other industrial or agricultural sectors, though typically the amounts required are far below what is produced and logistical problems limit this practice. The cost of landfilling is high, especially considering the stringent guidelines imposed by DWAF. Land disposal is another option that has potential, but requires that more research be conducted to assess the long-term viability of this approach.

### 1.2 Project background

This investigation formed a component of a larger study that encompassed a number of aspects relating to the assessment and remediation of metalliferous wastes from mining and processing activities. The project was initiated when the sponsors (BHP-Billiton) approached the Soil Science Discipline at the University of KwaZulu-Natal (UKZN), Pietermaritzburg, South Africa, requesting that research be conducted at three sites, all with industrial processing wastes. The sites were a decommissioned Pb/Zn mine (Pering Mine), an active Mn-smelter (Samancor) and an active Mn electro-winning plant (Manganese Metal Company, MMC). The primary interest at each site was the waste

residue produced during ore extraction and processing, namely the tailings dam at the Pering Mine, the Mn-rich siliceous-slag at Samancor and the Mn-rich filter-cake waste at MMC.

Of primary concern, to the sponsors, were the likely environmental risks associated with the wastes and extent of contaminant dispersal from the sites. In addition, consideration was given to some remediation strategies i.e., revegetation (specifically phytoremediation), electro-kinetic remediation and (later) land disposal. The extent of contaminant dispersal from each site and the use of electro-kinetic remediation technology to clean the waste were assessed in separate investigations and are not reported on here. This work focused on the use of revegetation and land disposal as means of remediating the unfavourable characteristics of the waste investigated. While initially phytoremediation (in particular, the use of hyperaccumulating plant species) was considered the primary focus of the study, it soon became evident that suitable plants for use at the Pering Mine were neither readily available nor ideally suited for use at this site. The nature of the tailings material and general environmental conditions of the area suggested that the use of endemic plants may be better suited if long-term sustainability was to be attained. The waste materials produced at the Samancor Mn-smelter and the MMC plant were not suited for phytoremediation because (1) both the disposal sites were still active; and (2) the inputs and treatment of the substrates required to alter the conditions for plant growth were not practicable or viable.

This led to a redevelopment of the project's original aims and objectives. At Pering Mine, revegetation of the tailings dam was considered with emphasis on using indigenous grass species. In addition, consideration was given to chemically-enhanced phytoremediation of the tailings dam. The slag produced at the Samancor Mn-smelter and the MMC waste were investigated with a view to using land application as a means of disposing of these wastes.

Thus this work investigates two major aspects that are relevant to the mining and industrial sector, namely: reclamation (specifically revegetation) and disposal (specifically land disposal) of metalliferous processing wastes. Revegetation of a waste heap aims to reduce the dispersal of contaminant from the waste, whilst creating a sustainable, aesthetically pleasing and functional landscape. Land application is, effectively, a low-cost disposal option based on the principle of diluting the waste (and associated risk factors) in a

medium (typically soil) that may further mitigate any negative aspects of the waste on the environment.

### **1.3 Aims and objectives**

The overall aims and objectives of the study were to characterise the wastes and evaluate the likely problems associated with each of the remediation approaches selected and test the feasibility of the approaches under laboratory and glasshouse conditions. The aims and objectives of each part of this work (Part 1 and Part 2) differed slightly.

In Part 1 the aims and objectives were:

- to introduce the philosophy of reclamation and present an overview of the general problems and reclamation approaches used in the reclamation of metalliferous mine tailings as well as outlining the current legal framework in South Africa (Chapter 2);
- to review the literature regarding the characterisation and reclamation of Pb/Zn mine tailings (Chapter 3);
- to characterise the tailings material from the Pering Pb/Zn Mine and define the limiting factors for purposes of revegetation (Chapter 4);
- to investigate the growth performance and growth-limiting factors of a variety of grass species grown in the tailings material using only inorganic fertilisation (Chapter 4); and
- to determine if the use of chemical amendments to enhance metal mobility could induce hyperaccumulation of selected metals in some grass species grown in the tailings material (Chapter 4).

The aims and objectives of Part 2 were:

- to introduce the concept and considerations for land disposal of waste (Chapter 5);
- to characterise the slag at Samancor and the electro-winning waste at MMC to determine the likely risk associated with land application of these wastes (Chapter 6);

- to investigate the effect of the slag and electro-winning waste, on selected chemical properties, when applied to six soils of contrasting characteristics (Chapters 7 and 8);
- to investigate the performance of ryegrass grown in selected soils treated with the wastes (Chapter 9); and
- to investigate some ameliorative treatments to reduce the problems associated with the application of these wastes to soils (Chapter 9).

Chapter 10 presents the final discussion and conclusions along with consideration of further research needs.

# **PART 1**

## **THE POTENTIAL OF SELECTED GRASS SPECIES TO REVEGETATE TAILINGS FROM A LEAD/ZINC MINE IN SOUTH AFRICA**

## CHAPTER 2

### THE RECLAMATION OF MINE TAILINGS: AN OVERVIEW

#### 2.1 General introduction

Mining activities often result in derelict landscapes and environmental degradation. This includes the impact of opencast and strip-mining practices, while ore processing residues, gangue and waste rock piles and tailings are frequently sources of heavy metal pollution due to dispersion by wind and water into the surrounding environment (Hossner and Hons, 1992; Tordoff *et al.*, 2000). The range of properties exhibited by the various wastes is vast and while generalisations about their properties can be made, the exact characteristics of a mine waste are site specific (Tordoff *et al.*, 2000). The following discussion presents a consideration of the philosophy of mine reclamation, a brief outline highlighting the main concerns surrounding metalliferous mine tailings and their reclamation, and an overview of the legal requirements for mine reclamation in South Africa. For the purposes of this discussion, tailings are defined as “the solid waste products of the milling and mineral concentration process that are considered too poor to be treated further, as opposed to the concentrates. Tailings are the finely ground host rock materials from which the desired mineral values have been extracted” (Barnhisel *et al.*, 2000).

A number of terms are used to describe various facets of mine waste reclamation, including remediation, rehabilitation, revegetation, restoration and replacement. Li (2006) suggests that, in the context of mining, the term “reclamation” refers to the general process whereby the mined wasteland is returned to some beneficial use, “restoration” to the reinstatement of the pre-mining ecosystem in terms of structural and functional aspects, “rehabilitation” refers to the process of reinstating the original ecosystem; and “replacement” to the creation of an alternative ecosystem to the original. Revegetation refers specifically to the process of establishing vegetation. Munshower (1994) assigns similar definitions to the terms restoration, reclamation, rehabilitation and revegetation to those of Li (2006), though suggests that reclamation and restoration are synonymous. In this document the terms will be used interchangeably, with some terms taking preference depending on the literature being reported (e.g. “revegetation” for plant growth studies).



## 2.2 The philosophy of reclamation

It may be asked if there is a need for the reclamation of mined land. A number of reasons can be forwarded, ranging from emotive responses and social considerations to academic perspectives. Perhaps the most fundamental sentiment is that land is a valuable and scarce resource that should be preserved with a great deal of care (Bradshaw and Chadwick, 1980). The moral requirement of this sentiment is in the notion that we have limited resources and it is only ethical that consideration be given to future generations that may need the same resource. The ethical aspect also encompasses the idea that as we are ‘taking’ from the Earth, we should ‘give back’. While we are unlikely to ever return what was removed, effort can be made to reduce both the short and long-term impact of our activities. Regardless of the reason for a specific mining activity there is a growing public awareness that the environment is the responsibility of everyone.

Environmental protection has become a part of the laws of many countries (Tordoff *et al.*, 2000). In South Africa, the Constitution, containing the Bill of Rights, gives environmental rights to all South Africans (Kidd, 1997). The Constitution states that “everyone has the right to (a) an environment that is not harmful to their health or well-being; (b) have the environment protected, for the benefit of present and future generations, through reasonable legislative and other measures that (i) prevent pollution and ecological degradation; (ii) promote conservation; and (iii) secure ecologically sustainable development and use of natural resources while promoting justifiable economic and social development”. Thus it has become a legal requirement to restore any form of degradation, thereby forcing mines to ‘clean up their act’. Bradshaw and Chadwick (1980) have also suggested that degraded environments have a negative impact on the behaviour of man, where the deterioration of the environment engenders a less responsible attitude for that environment which can ultimately lead to a breakdown of social well-being and economic collapse of that community.

## 2.3 General concerns and reclamation approaches

Hossner and Hons (1992), Munshower (1994) and Li (2006) summarise the limitations of tailings reclamation. They list acidity, salinity and/or sodicity, low soil fertility, toxic ions, physical limitations and dust as the main concerns. The impacts of these factors are well

documented in texts relating to mine reclamation (e.g. Munshower, 1994; Barnhisel *et al.*, 2000). The specific concerns relating to Pb/Zn mine tailings are presented in Chapter 3.

Some authors suggest that natural restoration of a site will occur if given sufficient time (Munshower, 1994; Bradshaw, 2000), though Li (2006) is of the opinion that this does not always occur, especially on some of the more toxic tailings. Li (2006) comments that, for the restoration of metal-mined tailings dams to occur within a reasonable timeframe, some form of human intervention is required. The intervention applied at a site is dependent on the specific conditions of the tailings, climatic factors and the designated end-use of the site. The typical order of intervention is topographic alteration, amelioration of substrate (to improve negative aspects), preparation of the site for revegetation, selection of suitable vegetation for use at the site, vegetation establishment and management of the site until it is self-sustainable (Bradshaw and Chadwick, 1980; Munshower, 1994; Li, 2006).

There are effectively two approaches used to ameliorate tailings material. One is the incorporation of ameliorants into the surface layers of the tailings; the other is the covering (or capping) of the tailings with less noxious media (Li, 2006). Typical ameliorants for incorporation and/or covers include inorganic fertilisers (usually N, P and K), lime (and liming agents), organic matter (e.g. manures, sewage sludge, straw/hay, composts, organic domestic refuse, paper-mill waste, etc.), industrial by-products (e.g. fly-ash), gypsum, rock/gravel mulches and, if available, topsoil (or mixed soil horizons) (Bradshaw and Chadwick, 1980; Munshower, 1994; Tordoff *et al.*, 2000) used singularly or in combination.

Once the substrate conditions have been altered, either by incorporation or capping, the next step is to establish a vegetative cover. Tordoff *et al.* (2000) and Li (2006) suggest that the establishment of vegetation is the preferred method of tailings stabilisation (also known as phytostabilisation). This approach is frequently used in conjunction with more traditional methods of contaminant stabilisation, such as liming or the use of phosphate compounds to bind metals (Prasad, 2003, Prasad and Freitas, 2003). Furthermore, vegetation has a high capacity to increase water removal from tailings (by evapotranspiration), potentially reducing the leaching of toxic elements and can be effective at reducing surface erosion, as roots bind the substrate and foliage reduces rainfall impact and reduces the velocity of surface water flow. Vegetation is also considered to be

more aesthetically pleasing than many other stabilisation techniques, better integrating the disturbed landscape into the surrounding environment.

Ideal plants for use in the stabilisation of contaminated soils and wastes are typically easily propagated and established, grow fast, have extensive root systems and are tolerant or adapted to adverse substrate conditions that include elevated contaminant levels and poor physical and fertility characteristics (Prasad and Freitas, 2003). These plants should have low root to shoot translocation of substrate contaminants. They should also lend themselves to traditional agricultural practices, for ease of establishment (Prasad and Freitas, 2003).

The selection of species for revegetation purposes may include the use of plant species that are adapted to local environmental conditions (Tordoff *et al.*, 2000), the use of leguminous plants to improve N cycling in the tailings, (Munshower, 1994; Mays *et al.*, 2000; Tordoff *et al.*, 2000; Li, 2006), the establishment of trees (Mays *et al.*, 2000) and the use of metal tolerant plants (metallophytes) (Hossner and Hons, 1992; Tordoff *et al.*, 2000; Li, 2006).

#### **2.4 Tailings restoration: A legal perspective**

A number of laws are in place in South Africa to protect the environment prior to, during and after mining. The legislation does not specifically target any particular type of mining waste, but is more holistic in its approach, with specific requirements for a mine set by the prevailing authorities. The most notable legal requirements are found in sections of the Minerals Act (50 of 1991) and, more recently, the Mineral and Petroleum Resources Development Act (MRPDA, 28 of 2002), but also include sections of the National Water Act (NWA, 36 of 1998), the National Environmental Management Act (NEMA; 107 of 1998), the Environmental Conservation Act (ECA; 73 of 1989) and the Air Quality Act (39 of 2004; still to be promulgated). The legislation gives no specific details on reclamation procedures, but rather prescribes principles, measures and regulations that should be adhered to when implementing the legal policy, where specific requirements are laid down by the local authority.

The NWA and NEMA do not specifically target the industrial sector, but promote a ‘duty of care’ philosophy to prevent pollution, where the polluter will be liable for any costs of

rehabilitation and any damages caused by pollution. Section 19 of the NWA (Part 4) deals with pollution prevention and, in particular, the situation where pollution of a water resource might result due to activities on land. It requires that the person who owns, controls, occupies or uses the land that is the source of the pollution is responsible for the measures to prevent pollution of water resources. The Act allows the catchment management agency concerned to take the necessary steps to prevent or remedy the effects of the pollution along with reasonable cost recovery from the persons responsible for the pollution. The Act specifically requires, *inter alia*, that where an activity is causing pollution, that the activity be managed in such a manner to prevent further pollution, that the activity complies with prescribed waste standards or management practices, that the activity be modified to either contain or prevent the movement of pollutants or eliminate any source of pollution and the responsible party remedy the effects of any pollution.

Section 28 (1) of NEMA states “Every person who causes, has caused or may cause significant pollution or degradation of the environment must take reasonable measures to prevent such pollution or degradation from occurring, continuing or recurring, or, in so far as such harm to the environment is authorised by law or cannot reasonably be avoided or stopped, to minimise and rectify such pollution or degradation of the environment”. This implies that, in the case of mined land, the waste materials be treated in such a manner so as to prevent them causing harm to the environment.

The Air Quality Act contains two sections that impact on reclamation of mine wastes, namely the control of dust (Section 32) and rehabilitation when mining operations cease (Section 33). Section 32 indicates that the Minister can prescribe measures to control dust from a site or activity, and steps to be taken to prevent dust and measures to control dust. Section 33 requires that notice be given to the Minister if cessation of mining operations is likely and of the plans that are in place or that have been considered for the rehabilitation of the mined area after mining operations have ceased and the prevention of atmospheric pollution after operations have stopped.

The Minerals Act (Section 38) requires that a mine rehabilitate its environment in accordance with an approved environmental management plan (EMP), as an integral part of, and simultaneously to, mining activities, and to the satisfaction of the Director (Mineral Development) concerned. Regulation 5.12 provides guidance for the stockpiling of topsoil

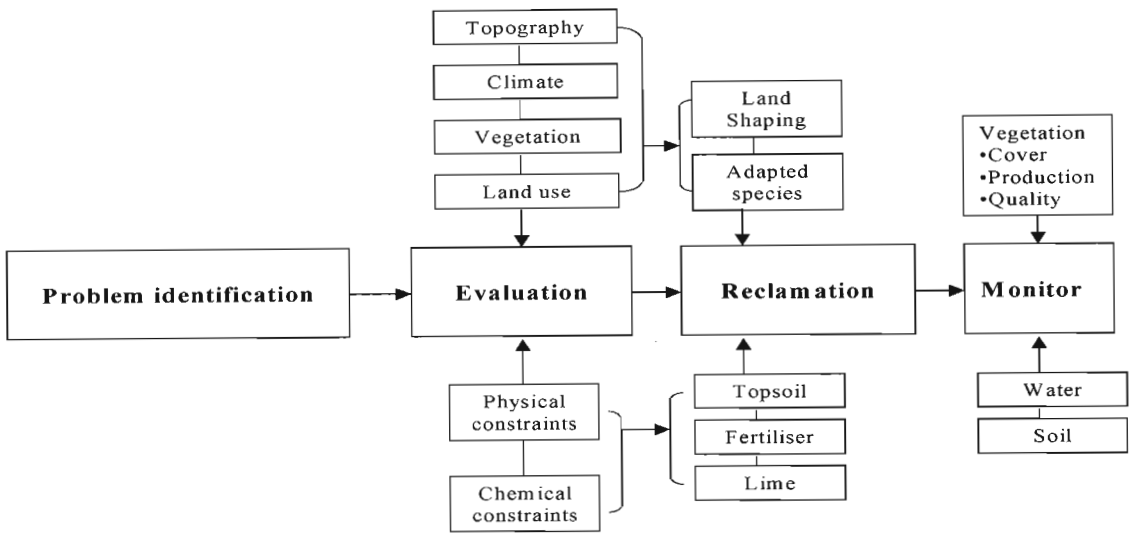
(defined as “all cultivatable soil that can be removed mechanically to a depth of one metre without blasting”; Regulation 5.11(e)). This requires that all topsoil be “removed from an opencast mine for purposes of prospecting or working, and that this topsoil be deposited at a specially selected site for replacement during rehabilitation of the disturbed surface”. Regulation 5.13.2 requires that where vegetation was disturbed for the purposes of mining, such vegetation shall be “...re-established to the satisfaction of the Director (Mineral Development), who may introduce a programme according to which the rehabilitation shall be done”.

Section 38 of the MPRDA (Parts 1d and e) states that the permit holder “...(a) must as far as is reasonably practicable, rehabilitate the environment affected by the mining operation to its natural or predetermined state or to a land use that conforms to the generally accepted principles of sustainable development; and (b) is responsible for any environmental damage, pollution or ecological degradation as a result of the mining operations both within and outside the boundaries of such an operation”. Section 39 of the MRPDA (Part 3a) requires that, in the preparation of an EMP, the baseline information concerning the affected environment be included to determine protection, remedial measures and the environmental management objectives. Part 3b(i) requires that the potential impact of the mining operation or activity on the environment be investigated and Part 3d that the EMP include information and descriptions of the actions that will be taken to prevent or remedy the effects of pollution as a result of the activity. Section 43 states that “a holder of a mining right or permit will be liable for all environmental liability, pollution, ecological degradation and the management thereof until the Minister issues a certificate of closure to the holder concerned”. A closure certificate will only be issued when the Chief Inspector and the Department of Water Affairs and Forestry confirm, in writing, that all the provisions pertaining to the health and safety and management of pollution to water resources have been addressed.

## 2.5 Conclusions

As public awareness of environmental issues grow, the need for reclamation of metalliferous mine wastes to a high standard increases (Tordoff *et al.*, 2000). Metalliferous mine tailings are typically devoid of vegetation and unproductive, as well as being sources of environmental contamination. They also tend to be aesthetically unacceptable. It would

seem that revegetation offers the best long-term and cost-effective solution to reclaiming metalliferous tailings. This approach is not without drawbacks as remediation of adverse substrate conditions can be difficult and the availability of species suitable for a specific site might be limited. Hossner and Hons (1992) present a scheme for the evaluation and reclamation of mine tailings (Figure 2.1).



**Figure 2.1** Idealised systematic approach for the evaluation and reclamation of mine tailings (adapted from Hossner and Hons, 1992).

The establishment of specific reclamation strategies is difficult, as the nature of the tailings can be highly variable. Thus it is necessary to assess, on a site-by-site basis, the exact conditions that are present and remedial action to be taken given the specific issues of concern. It is probable that the approaches used at different sites can be adapted for use at new sites so long as consideration is given to the differences between the sites and the approach adapted accordingly. Indeed this strategy may offer considerable savings in cost and time as it may reduce the research and development time required to find suitable remediation strategies for reclamation of tailings dams.

## CHAPTER 3

### CHARACTERISTICS AND RECLAMATION OF LEAD/ZINC MINE TAILINGS

#### 3.1 Introduction

South Africa has about three million tons of Pb-deposits and 15 million tons of Zn-deposits (Chamber of Mines of South Africa, 2006). Both Pb and Zn are generally mined as sulphide minerals, typically galena (PbS) and sphalerite (ZnS; Adriano, 1986; Fergusson, 1990), though other minerals may also be mined where economically viable. Cadmium and Cu may also be found in association with galena and sphalerite minerals (Fergusson, 1990). Both Pb and Zn are used extensively in the industrial sector (Adriano, 1986). Lead is used primarily for the manufacture of lead-acid batteries and also in paint pigments, solder and as an anti-knock agent in fuels (though this use has declined in recent times). Zinc is used as a metal additive to produce certain alloys, as an anti-corrosion coating on metals and in the manufacture of a variety of chemicals and automotive and electronic components.

The fate of Pb, Zn, Cd and Cu (and other metals) has been the focus of many studies due to environmental concerns over toxicity to both plant and animal life (Logan, 2000). Adriano (1986) indicates that both Pb and Cd are non-essential to both plant and animal life, but can cause toxicological effects. Copper and Zn are essential nutrients for plant and animal life, but at high concentrations may lead to toxicity. It is not the purpose of this document to review the chemical behaviour of Pb, Zn, Cd and Cu in the environment, and for such information the reader is referred to a number of texts that review trace element behaviour in the environment (Adriano, 1986; Fergusson, 1990; McBride, 1994; Ross, 1994; Kabata-Pendias, 2001; Sparks, 2003; Essington, 2004)

#### 3.2 Characteristics of lead/zinc mine tailings

Wastes from metalliferous mines are generally recognized as being environmentally hazardous due to high concentrations of potentially toxic elements (Tordoff *et al.*, 2000). Lead/Zn mines are no exception, where high levels of these elements may pose serious environmental risks. In addition high concentrations of S may exacerbate problems

(Hossner and Hons, 1992) in association with low pH, low organic matter content, high electrical conductivity (EC), low fertility and poor physical properties (Hossner and Hons, 1992; Ye *et al.*, 2000a and b). Much of the recent literature pertains to Chinese Pb/Zn mines, as vast tracts of land have been disturbed by mining operations in China. Ye *et al.* (2000a) estimate that, in China, about two million hectares have been left derelict by mining operations, many of these being Pb/Zn mines.

Typically the pH of Pb/Zn mine tailings have been reported to be near-neutral, but values ranged from very acidic (1.6) to alkaline (8.6) (Table 3.1). Generally, the EC of the tailings were high ( $> 200 \text{ mS m}^{-1}$ ), indicating potential salinity problems (Table 3.1). Organic carbon (OC) contents were generally low, typically  $< 1 \text{ g } 100\text{g}^{-1}$  (Table 3.1). However, in some cases, the elevated OC contents could be attributed to vegetation growing on the tailings dam (e.g. Ye *et al.*, 2002). Generally the total N concentrations were low ( $< 700 \text{ mg kg}^{-1}$ ), though some sites had elevated concentrations (e.g. Ye *et al.*, 2000a). Total P concentrations were also variable ranging from 52 to  $4\,400 \text{ mg kg}^{-1}$  (Table 3.1).

The principal elements of concern in most of the studies on Pb/Zn mine tailings have been Pb, Zn, Cu and Cd. In some instances authors report on other elements and nutrients (e.g. Fe, Mn, K), but as these are usually not the primary focus of the investigations they are excluded from this discussion. As expected, total (typically  $\text{HNO}_3/\text{HClO}_4$  digestion) concentrations of Pb and Zn were generally high for all sites, while Cu and Cd concentrations were lower (Table 3.2).

Total metal concentrations do not necessarily reflect plant availability and potential mobility in the soil (Fergusson, 1990), and use of total concentrations as an estimate of risk should be done with caution. As Pb/Zn tailings are usually derived from sulphide minerals, and may contain pyrite, the potential for acid generation exists (Hossner and Hons, 1992). In extreme cases, where a large amount of acidity is generated, high concentrations of metals may be mobilised, which may be comparable to total metal values determined in the laboratory. However, as an immediate estimate of metal mobility, the diethylenetriaminepentaacetic acid (DTPA) method may be a more useful indicator as this will represent the more readily available fraction of metal for plant uptake (and potential leaching).



**Table 3.1** Some basic chemical properties of tailings from various lead/zinc mines

Source	Mine area	Sample	pH	Electrical conductivity (mS m <sup>-1</sup> )	Organic carbon (g 100g <sup>-1</sup> )	Total N ----- (mg kg <sup>-1</sup> ) -----	Total P
Conesa <i>et al.</i> (2006)	Belleza Mine, Spain		1.6 - 3.3	200 - 3600 <sup>‡</sup>	0.1 - 1.5	130 - 650	na
	El Gorguel Mine, Spain		5.7 - 7.9	200 - 3100 <sup>‡</sup>	0.1 - 1.0	70 - 260	na
	El Niro Mine, Spain		6.4 - 1.3	200 - 1800 <sup>‡</sup>	0.1 - 0.8	60 - 230	na
Kovács <i>et al.</i> (2006)	Gyöngyösrozi, North Hungary	a <sup>†</sup>	3.6 - 7.4	100 - 1050 <sup>††</sup>	na	na	na
		b <sup>‡</sup>	3.2 - 7.2	100 - 980 <sup>††</sup>	na	na	na
Ma <i>et al.</i> (2006)	Lechang, China		8.0	370 <sup>††</sup>	1.0	8	100
Yang <i>et al.</i> (2003)	Lechang, China		8.6	41 <sup>††</sup>	1.4	52.3	550
Shu <i>et al.</i> (2002)	Lechang, China		7.1	209 <sup>††</sup>	0.6	507	619
Ye <i>et al.</i> (2002)	Lechang, China	a <sup>§</sup>	7.4	600 <sup>††</sup>	1.9	700	3500
		b <sup>¶</sup>	6.5	770 <sup>††</sup>	0.6	300	1800
		c <sup>#</sup>	7.5	540 <sup>††</sup>	0.8	200	4400
Ye <i>et al.</i> (2001)	Fankou Mine, China		7.5	na	na	398	695
Ye <i>et al.</i> (2000a)	Lechang, China		2.4	1178 <sup>††</sup>	1.0	1325	447
Ye <i>et al.</i> (2000b)	Lechang, China		6.1	418 <sup>††</sup>	0.7	429	52

na

Data not available.

†

Sample from depth profile from saturated tailings.

‡

Sample from depth profile from unsaturated tailings.

§

Sample from vegetated tailings.

¶

Sample from sparsely vegetated tailings.

#

Sample from unvegetated tailings heap.

‡

Determined in saturated paste extract.

††

Determined in 1:2 soil:water extract.

††

Determined in 1:2.5 soil:water extract.

**Table 3.2** Diethylenetriaminepentaacetic acid (DTPA-extractable) and total concentrations (mg kg<sup>-1</sup>) of Pb, Zn, Cu and Cd in tailings from various lead/zinc mines

Source	Mine area	Sample	Pb		Zn		Cu		Cd	
			DTPA	Total	DTPA	Total	DTPA	Total	DTPA	Total
Conesa <i>et al.</i> (2006)	Belleza Mine, Spain		na	1300 - 17000	na	4760 - 15700	na	220 - 1400	na	na
	El Gorguel Mine, Spain		na	3800 - 6600	na	8980-14100	na	67- 180	na	na
	El Niro Mine, Spain		na	2700 - 9200	na	4830 - 23500	na	85 - 825	na	na
Kovács <i>et al.</i> (2006)	Gyöngyösorózi, North Hungary	a <sup>†</sup>	na	40-516	na	75-1890	na	70-452	na	na
		b <sup>‡</sup>	na	25-1540	na	63-4547	na	70-921	na	na
Ma <i>et al.</i> (2006)	Lechang, China		1202	4418	383	9827	3.5	90	bd	33
Yang <i>et al.</i> (2003)	Lechang, China		331	4164	187	4377	0.8	35	2.6	35
Shu <i>et al.</i> (2002)	Lechang, China		98	3123	101	3418	2.0	174	0.1	225
Ye <i>et al.</i> (2002)	Lechang, China	a <sup>§</sup>	59	1642	115	5021	12.0	192	1.5	14
		b <sup>¶</sup>	85	1260	106	5620	6.5	117	0.9	8
		c <sup>#</sup>	112	1019	200	6773	4.3	139	1.1	23
Ye <i>et al.</i> (2001)	Fankou Mine, China		44	5091	818	12563	5.4	91	1.8	35
Ye <i>et al.</i> (2000a)	Lechang, China		na	1042	na	2132	na	81	na	12
Ye <i>et al.</i> (2000b)	Lechang, China		196	na	79	na	na	na	na	na

na Data not available.  
<sup>†</sup> Sample from depth profile from saturated tailings.  
<sup>‡</sup> Sample from depth profile from unsaturated tailings.  
<sup>§</sup> Sample from vegetated tailings.  
<sup>¶</sup> Sample from sparsely vegetated tailings.  
<sup>#</sup> Sample from unvegetated tailings heap.

The concentrations of DTPA-extractable metals from the various tailings (Table 3.2) were considerably less than the total concentrations, ranging from less than 1% to more than 25% of the total Pb concentrations. The DTPA-extractable Zn formed a more consistent proportion of the total Zn, ranging from about 2 to 4% (Table 3.2). The concentrations of DTPA-extractable Pb were very high in some instances (e.g. Ma *et al.*, 2006; 1202 mg kg<sup>-1</sup>), suggesting the potential for plant toxicity.

Clevenger (1990) used a five-step sequential extraction to partition metals (Pb, Zn, Cd and Cu) into exchangeable, carbonate bound, Fe/Mn oxide bound, organic matter bound and residual in four Pb/Zn mine tailings from “The Old Lead Belt” southeast of Missouri (U.S.A.). It was found that Pb was primarily in the residual fraction, assumed to exist as sulphide species. This was attributed to the mineral forms that were not removed during ore processing, but that had not had sufficient time or atmospheric exposure to oxidise and react with other components of the tailings. Small amounts of Pb were also present in the Fe/Mn oxide-bound phase. Zinc, Cu and Cd were reported in most of the different fractions but primarily in the residual fraction. The author also reported that water leaching removed very little metal from the tailings. Clevenger (1990) warns that, while these metals are bound in unavailable forms, interactions with micro-organisms and chelating agents (organic matter) may increase metal mobility. Zhang *et al.* (2003) fractionated sediment samples, containing tailings from the Shanshulin Pb/Zn Mine (China), from an area dominated by carbonate-rich minerals and soils. They found that Pb was associated with carbonate and oxide minerals, while Cu and Zn were associated with sulphide and organic fractions, indicating that carbonate minerals may reduce Pb solubility in calcareous environments. They reported alkaline pH values (> 8) for all samples tested, indicating that dissolution of carbonate minerals would not be likely. Under these conditions it was expected that sorption of Pb onto carbonate mineral surfaces would be high.

Acidity is often a serious concern in sulphide mine wastes. The acidity generated in tailings results in increased solubility and mobility of minerals and metal ions, increasing the risk of both water and vegetation contamination. Tailings containing pyrite and other sulphide minerals can weather quickly to produce acid mine drainage (Kovács *et al.*, 2006). Pyrite undergoes oxidation and hydrolysis to generate sulphuric acid. Factors such as pH, partial pressure of O<sub>2</sub>, pyrite morphology, specific surface area, presence/absence of sulphide-oxidising bacteria, clay mineralogy as well as hydrological factors determine the

rate of pyrite oxidation (Kovács *et al.*, 2006). Details on these processes and influences can be obtained elsewhere (Carrucio *et al.*, 1988; Hossner and Hons, 1992; Ritcey, 2005). The acid-buffering capacity of tailings is controlled by quantity and types of aluminosilicates, carbonates and Al-, Fe- and Mn-hydroxides (Kovács *et al.*, 2006), which affect the acid-base behaviour and metal content of leachates.

Excess acidity is usually ameliorated using lime or liming agents. Hossner and Hons (1994) warn that, in the case of acidity due to weathering of sulphide minerals, the usual agricultural estimates of lime requirement may be an underestimate. For acid tailings, measures of acid-producing and acid-neutralising potential are required for accurate predictions of lime application rates. Shu *et al.* (2001) report on the acid-producing and acid-neutralising capacity of some Pb/Zn mine tailings from Lechang Mine, China. They found that the tailings had high acid-producing potential, while the acid-neutralising capacity was low. The acidification of the surface layer (0 to 200 mm) also led to increased concentrations of Pb, Zn, Cu and Cd deeper in the tailings dam (> 200 mm). This was attributed to higher rates of pyrite oxidation in the surface layer, leading to increased dissolution and leaching of metals. There was also an inverse relationship between the EC and pH of the acidified tailings, again attributed to the release of both cations and anions into the soil solution due to acidification in the surface layer of the tailings. Wong *et al.* (1998, cited by Ye *et al.*, 2000a) also report on the high acid-generating potential of Pb/Zn mine tailings with high S content. They found that the pH of the surface layer of a tailings dam decreased from 6.1 to 2.4 within 6 months after rototilling.

The mineralogy of tailings may influence the chemical behaviour of the material. However, little literature exists that describes the mineralogical nature of Pb/Zn tailings, though some articles report on this as part of the characterisation of the tailings studied. Kovács *et al.* (2006) indicated that the tailings they studied consisted predominantly of quartz, pyrite and K-feldspar (orthoclase), with trace amounts of sphalerite, galena, calcite, gypsum and aluminosilicates. Göktepe (2005) found that tailings from the abandoned Pb/Zn mines in the Bahesir region, Turkey, consisted predominantly of anglesite, hematite, quartz and calcite, suggesting a well-oxidised environment. Traces of sphalerite, pyrite, galena and chalcopyrite were also present.

Few authors report specifically on the physical properties of Pb/Zn tailings dams. Hossner and Hons (1992) and Tordoff *et al.* (2000) introduce some of the physical problems associated with tailings dams. The texture of tailings may vary from coarse to fine, depending on the mining processes and the design of the tailings dam. Often stratification occurs in the tailings pond, where coarser particles will settle nearer the inlet to the tailings dam, while finer material will settle in the ponding areas and near the outlets (Sidle *et al.*, 1991; Hossner and Hons, 1992). This stratification can lead to crusting and cracking when dry. The texture and degree of stratification can also lead to the creation of impervious layers within the tailings. High bulk density may also be a problem, where values above  $1.5 \text{ g cm}^{-3}$  may limit rooting volumes. Excessively high or low water holding capacities are also common, depending on the texture of the tailings. When dark coloured tailings are subject to solar radiation, surface temperatures may rise excessively, increasing evapotranspiration and desiccating seedlings. Where tailings tend to be finely divided particles, dust may be a major problem, polluting the surrounding environment by both wind and water dispersion of the particles (Hossner and Hons, 1992). Ye *et al.* (2002) report on the texture of various Pb/Zn mine tailings. The particle size distribution of the different tailings was variable, with textures ranging from silty-loam to sandy-loam and sandy. They concluded that the physical structure of the tailings was not suitable for the establishment of plants. Conesa *et al.* (2006) investigated three different Pb/Zn mine tailings and found that they all had low clay contents, being predominantly silt and sand. A similar situation existed for tailings reported on by Kovács *et al.* (2006).

It is clear that Pb/Zn tailings may exhibit unfavourable chemical and physical attributes, and pose a high risk to the surrounding environment. They also range in their characteristics, primarily due to differences in the mineralogy of the host rock and ore body, as well as the industrial processing techniques used to extract the ore. The extreme nature of many Pb/Zn tailings often requires dramatic remedial action, where single or combination treatments are used to alleviate some of the problems (Tordoff *et al.*, 2000). Generally the primary concern in these types of tailings is metal toxicity and low nutrient content. These problems are often associated with potential acidity and poor physical properties.

### 3.3 The reclamation of lead/zinc mine tailings

Various treatments have been proposed and tested by researchers to overcome some of the negative characteristics of Pb/Zn mine tailings. These include addition of amendments and ameliorants (e.g. lime, fertilisers, sludges, soil covers, microbiological inoculations), revegetation, construction of wetlands and combinations of these (Table 3.3).

A common practice with respect to revegetation of mined land is to use topsoil as a cover or cap over mine waste (Munshower, 1994). Zhang *et al.* (2001) investigated the potential of topsoil from an abandoned farmland as a seed source when applied as a cover on an acid tailings dam. The plants derived from the topsoil were considered for their phytoremediation potential. They report that the topsoil (10 mm depth) contained about 6850 seeds m<sup>-2</sup> from 41 different species. They found that regardless of depth of soil placed on the tailings (10, 20, 40 and 80 mm); no significant differences existed between emergent seedling densities in the different layer thicknesses. However, seedlings grown from the 10 and 20 mm thick soil layers died within 3 months of planting, plants in the 40 mm thick soil layer died within a year, while total vegetative cover was achieved in the 80 mm soil layer. The death of plants in the 10, 20 and 40 mm soil layers was attributed to the high acidity of the soil, derived from the acidic tailings material. The pH of the 80 mm soil layer also declined (6.7 to 5.4), but not sufficiently to cause plant death. They recommended that an additional subsoil layer be used to separate the topsoil from the tailings material to reduce the oxidation of pyritic material in the tailings. This would allow a thinner topsoil layer to be used. In the case of the 80 mm soil layer the dominant species, with respect to cover and biomass, was the leguminous shrub *Leucaena leucocephala*, with a number of ground-cover species also present. They found that Pb concentrations of the four dominant species recorded were in the range reported for plants growing in contaminated soil (30 to 300 mg kg<sup>-1</sup>), while concentrations of Zn and Cu were within the 'normal' or 'sufficient' range (27 to 150 and 5 to 30 mg kg<sup>-1</sup> for Zn and Cu, respectively). They concluded that woody legumes may be better suited for revegetation of tailings.

Ye *et al.* (2000b) grew *Cynodon dactylon*, *Agropyron elongatum*, *Lolium multiflorum* and *Trifolium repens* in tailings covered with varying ratios of pig-manure, mushroom compost, burnt coal residue, fly-ash, and topsoil. They found that adding a 100 mm thick layer of fly-ash or a 150 mm thick layer of burnt coal residue between the cover soil and

tailings was effective at improving plant growth, when compared to unamended tailings or treatments with no barrier layer. This was attributed to an increase in the pH of the soil cover layer as both the fly-ash and burnt coal residue had high pH (9.6 and 7.9, respectively). *Cynodon dactylon* grew well in all treatments, except for the unamended tailings, with 90 to 100% cover. Good growth of *A. elongatum* and *L. multiflorum* was only achieved in treatments with a barrier layer. *Trifolium repens* died soon after germination and was excluded from the trial. These authors report on Pb and Zn uptake by the three grass species, but do not discuss these in terms of the applied treatments. However, from the data presented it appears that generally the highest uptake of Pb occurred in the pig-manure and mushroom compost treatment with 150 mm topsoil. The use of a thicker soil layer (300 mm) and burnt coal residue and fly-ash reduced Pb uptake, in some instances significantly. A similar situation was noted for Zn uptake. They recommended *C. dactylon* for the revegetation of the tailings dam.

A number of researchers have investigated the potential of various amendments to improve the growth of plants in Pb/Zn mine tailings. Lan *et al.* (1998) investigated the effect of applying river sediment or domestic refuse (mainly paper and kitchen waste, aged for a year), at rates of 30, 60, and 90% ( $\text{m m}^{-1}$ ), over four levels of inorganic fertiliser, on the yield and metal uptake of *Stylosanthes guianensis* cv. *Graham* when grown in tailings from the Fankou Mine, China. They found that yield of the plants increased with addition of river sediment or domestic refuse, but not with inorganic fertiliser. In general, plants grown in tailings amended with 30 % river sediment accumulated the highest amounts of Pb, Zn, Cd and Cu.

Ye *et al.* (1999) tested the effects of lime and pig-manure on the growth of *A. elongatum* and *T. repens* grown in Pb/Zn mine tailings. The combined application of lime and pig-manure increased the pH and reduced the EC and DTPA-extractable concentrations of Pb, Zn and Cd of the tailings. Growth of both plant species was also improved. Addition of lime alone did not improve growth of either species, but supplemental N fertilisation enhanced shoot growth of *A. elongatum*. Lime and pig-manure did not reduce the uptake and accumulation of Pb, Zn and Cd in *A. elongatum*, but the higher pig-manure application rates significantly reduced the Pb content of *T. repens*.

Combination treatments of lime and manure compost improved the growth of *C. dactylon* and *A. elongatum* grown in tailings under greenhouse conditions (Ye *et al.*, 2000a). This was attributed to reductions in pH, EC and extractable metal concentrations. The highest yields were achieved with lime application rates of  $\geq 80 \text{ Mg ha}^{-1}$  and compost at  $100 \text{ Mg ha}^{-1}$ . At lime rates of 120 to  $160 \text{ Mg ha}^{-1}$  Zn uptake was reduced, but no change in Pb uptake was observed. *Cynodon dactylon* was also recommended for revegetation purposes as it was more tolerant of the unfavourable growth conditions. Ye *et al.* (2001) tested the growth of two leguminous plants (*Sesbania rostrata* and *S. cannabina*) in sewage sludge amended Pb/Zn mine tailings. They found that both species could survive for at least 80 days in unamended tailings, though growth was negatively affected. High rates of sludge incorporated in the tailings improved the growth of both species, and reduced uptake of Pb, Zn and Cd.

Shu *et al.* (2002) conducted a field experiment to test the growth of *Vertiveria zizanioides*, *Paspalum notatum*, *C. dactylon*, and *Imperata cylindrica* var. *major* in Pb/Zn mine tailings. The effect of applying inorganic fertiliser and domestic refuse (70 % coal-ash mixture) was also tested. For all grass species yield was improved with additions of either fertiliser or domestic refuse, but was highest in the combination treatment when compared to the control tailings. They found that after 6 months growth, regardless of treatment, *V. zizanioides* had the highest biomass, followed by *P. notatum*, *C. dactylon*, and *I. cylindrica*. Unfortunately uptake of metals by these grasses was not considered, but *V. zizanioides* was recommended for revegetation of these types of tailings. Chiu *et al.* (2006) found that addition of manure compost or sewage sludge increased the yield of *V. zizanioides* and *Phragmites australis* when grown in Pb/Zn mine tailings from the Lechang Mine in China. The addition of manure and sludge also reduced DTPA-extractable Pb and Zn in the tailings, increased levels of N, P and K, and reduced the uptake of Pb in the plants.

Most plant growth studies report on plant production and element uptake in relation to applied treatments, but few consider the impact of a mine waste on physiological aspects of plant growth. Pang *et al.* (2003) investigated some of the physiological aspects of using *V. zizanioides* on Pb/Zn mine tailings. They report that high proportions of Pb/Zn mine tailings in the growth substrate inhibited leaf growth, dry matter production and photosynthesis. They found that production and accumulation of proline and abscisic acid



was stimulated while activities of superoxidase dismutase, peroxidase and catalase were enhanced. This suggested that different physiological responses were taking place in different parts of the plant to reduce the toxicity effects of high metal concentrations. Additional N fertiliser applications also ameliorated the negative effect of high proportions of Pb/Zn mine tailings.

The ultimate goal of a revegetation programme is to create a self-sustainable ecosystem. In natural systems a number of biotic components are involved in the functioning of these systems, though this is seldom considered in disturbed environments. Ma *et al.* (2006) investigated the interactive associations between leguminous trees, arbuscular mycorrhizal fungi (AMF) and earthworms in Pb/Zn mine tailings from the Shaoguan, Guangdong Province of China. A glasshouse investigation was used to test the combined effect of earthworms (*Pheretima guillelmi*) and AMF (*Glomus sp.*) on the growth response of the leguminous shrub *L. leucocephala* grown in topsoil-amended tailings. They found that AMF were beneficial in improving N, P and K uptake by the shrubs, while earthworms alone had greater influence in improving N nutrition of the plants. The combined effects were reported to be synergistic where there was an increase in plant growth, greater uptake of N, P and K and a reduction in the uptake of toxic metals (Pb and Zn).

The addition of organic matter to mineral wastes may in some instances improve microbial activity within the waste, potentially improving conditions for plant growth. Romero *et al.* (2005) tested the potential of two organic amendments (fresh and composted olive-mill solid waste) to improve microbial activity and reduce metal mobility in tailings from a Pb/Zn mine in Spain. They measured the change in enzymatic activity and Pb and Zn availability in tailings incubated with the olive-mill wastes. They found that composted waste stimulated microbial activity, while fresh waste did not. This was attributed to the presence of polyphenols in the fresh olive-mill waste that inhibits enzyme activities. Lead and Zn availability increased with waste additions, attributed to the formation of soluble organo-metallic complexes. They conclude that the use of olive-mill waste to ameliorate tailings may have limited potential due to increased metal mobility.

Storing of sulphide-rich mineral wastes under water (or wetland conditions) has been suggested as a method to reduce the oxidation of the sulphide minerals and so reduce metal release into the soil solution (Jacob and Otte, 2004a; Yang *et al.*, 2006). Jacob and Otte

(2004b) report on the long-term (90 year) effect of submergence of tailings, under differing vegetative conditions, on metal availability. They compared dry areas of tailings (with no vegetation and low organic matter (OM)) to permanently flooded areas with either no vegetation and low OM, dead vegetation and low OM or living plants with high OM. They found that in flooded areas with living plants metal mobility was enhanced. This was attributed to radial oxygen loss from plant roots (root respiration) that caused oxidation of metal sulphides. Wet areas without vegetation and high OM had reduced metal mobility, but increased concentrations of acid-volatile sulphides. They concluded that, while reducing conditions created by flooding could reduce metal mobility, this could easily be altered by the introduction of plants and drying of the tailings, both potentially leading to enhanced oxidising conditions. In a similar, but short-term study (2.25 years), Jacob and Otte (2004a) reported similar effects, to those reported on by Jacob and Otte (2004b), in two different tailings. Yang *et al.* (2006) examined the ability of a 16-year-old constructed wetland to act as a filter on discharge from a Pb/Zn mine. They found that Cd, Pb and Zn concentrations in the outflow water from the wetland were 94, 99, and 97%, respectively, lower than inflow levels. They also found that the ability of the wetland to purify water was related to the maturity (age) of the wetland, where the purifying ability of the mature wetland (16-year-old) was greater than when it was newly established.

### 3.4 Conclusions

Tailings produced from the mining and processing of Pb and Zn ores typically have unfavourable chemical and physical characteristics. Factors such as acidity, salinity, poor fertility, compaction, and high concentrations of metals, notably Pb and Zn, are generally the primary issues of concern. In some instances high levels of other metals (Cd and Cu) are also reported.

Revegetation of tailings dams is necessary to reduce movement of pollutants to the surrounding environment, to improve the long-term stability of the tailings dams and to create an environment that is aesthetically appealing (Lan *et al.*, 1998). As plant growth is often limited by the negative characteristics of Pb/Zn mine tailings, the success of revegetation programmes is dependent on the ability of workers to ameliorate the negative characteristics of the wastes and on the selection of suitable cover species. The use of amendments or ameliorants (e.g. lime, fertiliser, compost, manure, sludges and sediments)

may be beneficial in reducing the noxious nature of the tailings or as a means to overcome deficiencies within the tailings. Addition of fertiliser can improve the nutrient status of tailings, though some authors report no difference in plant growth after inorganic fertiliser addition (Lan *et al.*, 1998). Typically, addition of organic amendments improves plant growth (e.g. Lan *et al.*, 1998; Ye *et al.*, 1999, 2000a and b, 2001). However, use of organic wastes may lead to the formation of organo-metallic complexes that increase metal mobility in the tailings (Romero *et al.*, 2005), possibly leading to groundwater contamination and increased metal uptake by plants.

Storing of tailings under wetland conditions appears viable as a means to reduce metal mobility, but requires a permanent supply of water. Furthermore, addition of plants may increase metal availability in the tailings due to radial oxygen loss from plant roots. The ability of wetlands to purify contaminated water is well documented (Sheoran and Sheoran, 2006) and has been reported to work in the case of discharge from Pb/Zn mine tailings (Yang *et al.*, 2006):

While many researchers have reported on the benefits of using various amendments and strategies to remediate Pb/Zn tailings, the application of these approaches may have limited value in the case of the Pering Mine. Both logistical and economic constraints do not allow for the importation of sufficient amounts of organic amendments, and the climate will limit the types of vegetation that can be grown in this region. As was indicated in Chapter 2, the use of plant species adapted to a particular environment may improve the success of revegetation programme. This, in conjunction with suitable ameliorants, may offer the most cost-effective, long-term solution to revegetating derelict mine-dumps.

In the following investigation (Chapter 4) the tailings from Pering Mine are comprehensively characterised and the performance of six grass species assessed when grown in tailings treated with varying levels of inorganic fertiliser. An additional investigation was conducted to assess the potential for chemically-enhanced removal of metals from the tailings by three of the grass species.

## CHAPTER 4

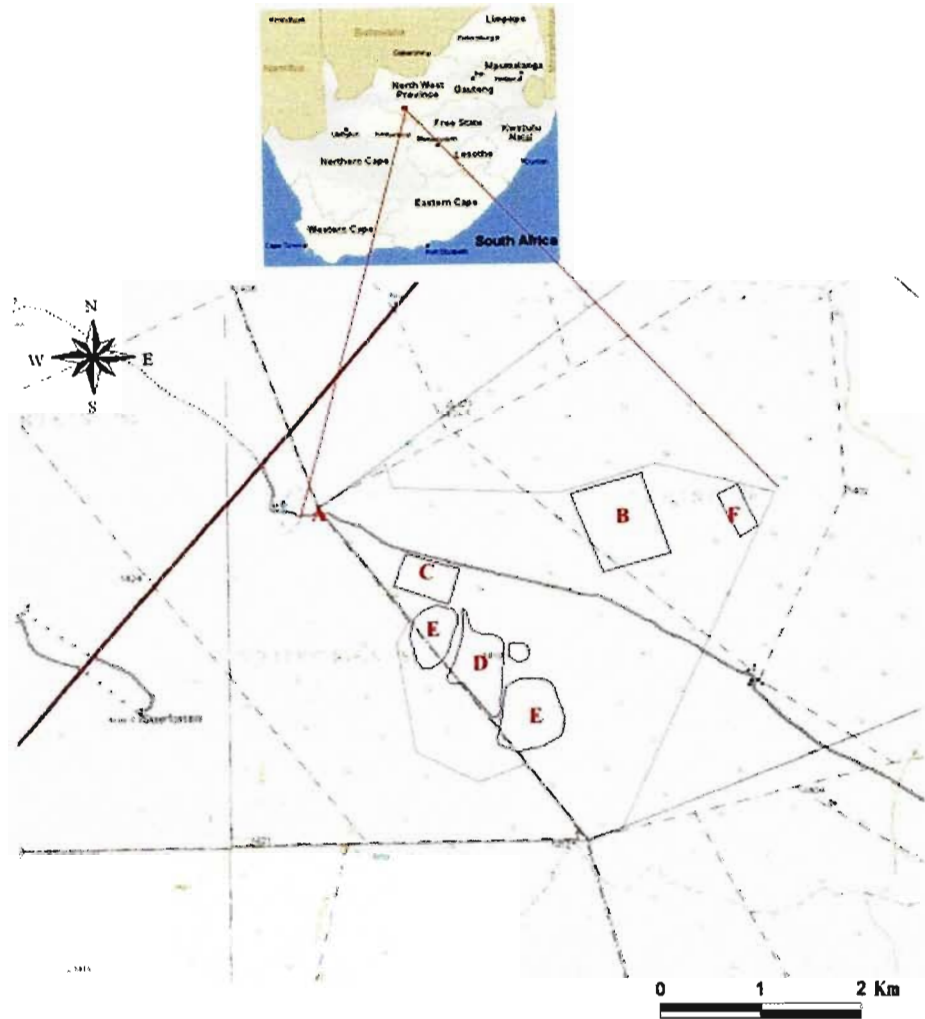
### REVEGETATION OF LEAD/ZINC TAILINGS FROM PERING MINE

#### 4.1 Introduction

Pering Mine (Map 4.1) is located approximately 18 km north-east of Reivilo in the North West Province of South Africa (27°26' South; 24°16' East). The mine is situated on the Ghaap Plateau at an altitude of approximately 1 400 m amsl. The region has an arid climate with a highly variable summer rainfall pattern (mean annual rainfall: 412.3 mm; range: 314.0 to 513.2 mm; Memoirs on the Agricultural Natural Resources of South Africa, 1986).

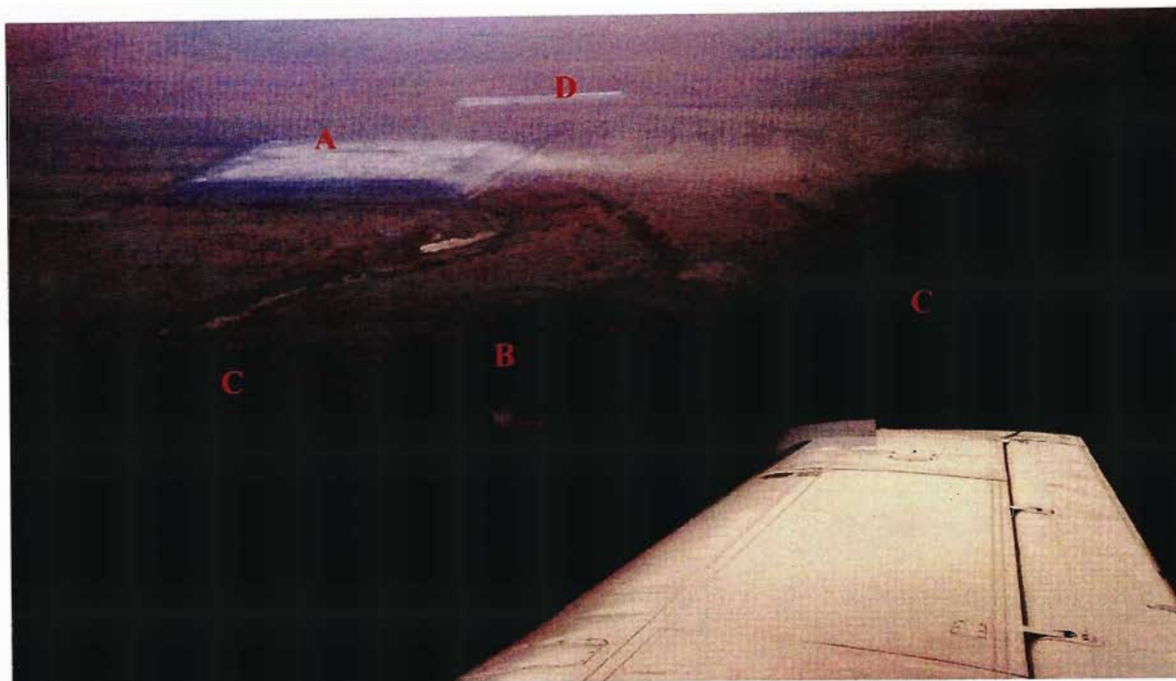
The principal shrubs in the region are *Tarchonanthus camphoratus*, *Rhizogium trichotum*, *Ehretia rigida*, *Grewia flava*, *Maytenus heterophylla* and *Rhus lancea* (Acocks, 1988; Low and Rebelo, 1996). The tree layer is less dominant and consists of *Olea europea*, *Acacia tortilis* and *Boscia albitrunca* (Low and Rebelo, 1996). The predominant grass species are *Themeda triandra*, *Aristida diffusa*, *Stipagrostis uniplumis*, *Cymbopogon plurinodis* and *Digitaria eriantha*. The veld also includes other less dominant species, such as *Fingeruthia africana*, *Eragrostis superba* and *Cenchrus ciliaris* (Acocks, 1988; Low and Rebelo, 1996).

The Pering Mine was an opencast pit mine where the ore-deposit was found in a small basin-like feature about 2 km in diameter (du Toit, 1998). About 18 000 Mg of ore with a combined grade of about 4 % lead and zinc were mined (du Toit, 1998). The predominant minerals were galena and sphalerite, with a lead to zinc ratio of between 5:1 and 2:1 (du Toit, 1998). Minor traces of pyrite (FeS) and chalcopyrite (CuS) were also present, but not at economically valuable concentrations. The minerals were concentrated in an almost horizontal carbonate layer, primarily dolomite, of the Lower Proterozoic Reivilo Formation (du Toit, 1998). Mining operations ceased in November 2002 and ore processing was terminated in early 2003.



**Map 4.1** Location of Pering Mine in South Africa and an expanded view of the site layout, where A) is the entrance to the mine site; B) the tailings dam; C) the office block and ore processing section; D) the main pit; E) the rock piles; and F) the water return dam.

Lead and Zn minerals were removed from the dolomitic matrix by froth flotation. The residue slurry was pumped into the tailings dam, which is the primary focus of this investigation. It is situated in the north-eastern part of the mine property (Map 4.1, Plate 4.1). The average depth of the tailings dam was about 30 m, with a basal footprint area of about 522 000 m<sup>2</sup>. The volume of the tailings dam is approximately 12 100 000 m<sup>3</sup>, this equating to about 20 570 Mg of tailings material (based on a bulk density of 1.7 g cm<sup>-3</sup>).



**Plate 4.1** Aerial photograph of Pering Mine, showing A) the tailings dam; B) the main pit; C) the rock piles; and D) the water return dam. Photograph courtesy of BHP-Billiton Johannesburg Technology Centre.

## 4.2 Characterisation of tailings from Pering Mine

### 4.2.1 Materials and methods

#### 4.2.1.1 *Waste material collection and preparation*

A bulk sample of Pering Mine tailings material (PT) was collected from the top of the tailings dam (sample 1). Material from the upper 500 mm was shoveled into 50 kg nylon bags and transported to the University for further handling. An additional sample (2) was collected from the side of the tailings dam to assess the variability in total elemental composition of the PT (see Section 4.2.1.4). The PT was air-dried, thoroughly mixed, and milled (by rolling with metal-roller) to pass through a 2 mm sieve, though the material was naturally fine, a result of the crushing process used for ore extraction. All analyses and pot experiments were conducted on < 2 mm material of sample 1. Analyses were conducted in triplicate (unless otherwise indicated) and the mean results are reported.

#### 4.2.1.2 *Chemical characteristics*

Electrical conductivity (EC) and pH were measured in distilled water using a Radiometer CDM83 electrical conductivity meter and a Radiometer PHM210 pH meter with a standard glass electrode, respectively. A PT:solution ratio of 1:2.5 was used (10 g PT:25 mL solution), and left to stand for about 45 minutes with occasional stirring using a glass rod. The pH was also measured in 1 M KCl using the same PT:solution ratio as for the water extract. Extractable base cations (Ca, K, Mg and Na) were determined by saturating with  $\text{NH}_4^+$  (1 M ammonium acetate, pH 7) and cation exchange capacity (CEC) by subsequent replacement with  $\text{K}^+$  (Soil Classification Working Group, 1991). Calcium, K, Mg and Na concentrations were determined by atomic absorption spectrophotometry (AAS, Varian SpectrAA-200) and  $\text{NH}_4^+$  concentrations by steam distillation (Bremmer and Mulvaney, 1982), using a Gerhardt Vapodest 1.

Nitrate and ammonia were extracted with 2 M KCl (Maynard and Kalra, 1993) and solution concentrations determined colorimetrically using a TRAACS 2000 continuous flow auto-analyser. Total N was determined by Kjeldahl digestion and  $\text{NH}_4^+$  by distillation (Bremmer and Mulvaney, 1982). Plant available phosphorus was estimated by extracting with AMBIC solution (0.25 M ammonium bicarbonate, pH 8.3) and P was determined colorimetrically (The Non-Affiliated Soil Analysis Work Committee, 1990) on a Varian Cary 1E UV-Visible spectrophotometer (UV-Vis). Calcium carbonate equivalence (CCE) was measured according to Jackson (1958). Organic carbon (OC) was determined titrimetrically following potassium dichromate oxidation on < 0.5 mm material (Walkley, 1947).

Total elemental concentrations and loss on ignition (L.O.I.) were determined by X-ray fluorescence spectrometry. Plant available (DTPA-extractable (pH 7.3)) Cd, Cu, Cr, Mn, Fe, Ni, Pb and Zn were determined by the method of Liang and Karamanos (1993). Elemental solution concentrations were determined by AAS. Adaptations of the toxicity characterisation leaching procedure (TCLP) and acid rain procedure (DWAf, 2005) were used to determine the potential of metal leaching from the PT and risk associated with these metals. The TCLP method involved extracting the waste with TCLP solution number 2 (5.7 mL glacial acetic acid, pH 2.88) and the acid rain procedure involved extraction with  $\text{CO}_2$ -saturated, distilled water (carbonic acid solution, pH adjusted to between 3.6 and 3.8

with  $\text{HNO}_3$ ). The same PT:solution ratio was maintained as recommended in the method (1:20), though the mass of sample was reduced from 100 g to 1 g, for practical purposes. Extracts were analysed for Cd, Cu, Cr, Mn, Fe, Ni, Pb and Zn by AAS. The pH of the extracts was also measured.

Water-soluble elements (Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S and Zn) were determined in saturated paste extracts (United States Soil Salinity Laboratory Staff, 1954) by inductively coupled plasma emission spectrometry (ICP, Varian Vista MPX). The EC of the extracts was also determined.

#### 4.2.1.3 *Physical characteristics*

Particle size distribution was determined by an adaptation of the pipette method (Gee and Bauder, 1986; Appendix 4.1). Particle density was determined according to the method of Blake and Hartge (1986). Bulk density of the upper 50 mm of the tailings dam was determined from core samples ( $n = 5$ ; Moodley, 2001).

#### 4.2.1.4 *Mineralogy*

X-ray diffraction analysis on random powders (sample 1 and 2) was carried out on a Philips PW1050 diffractometer using monochromated  $\text{Co K}\alpha$  radiation, from  $3^\circ$  to  $75^\circ 2\theta$  with a scanning step of  $0.02^\circ$  at  $1^\circ$  per minute counting interval. The diffraction data were captured by a Sietronics 122D automated micro-processor attached to the X-ray diffractometer. The samples were then qualitatively analysed to determine major mineralogical components.

Waste materials were also examined by environmental scanning electron microscopy (ESEM, Philips XL 30). Qualitative chemical composition was determined by energy dispersive X-ray microanalysis (EDX) and the data interpreted using the EDAX<sup>®</sup> Phoenix software (Revision 3.2).



4.2.1.5 Phosphorus sorption

The P sorption capacity was determined using an adaptation of the method presented by Rowell (1994). Twenty-five mL of a range of P solutions (0, 1, 2, 4, 8, 16, 32 and 64 mg P L<sup>-1</sup>) were added in a 0.01 M CaCl<sub>2</sub> matrix to 0.5 g of PT. The mixtures were shaken end-over-end (30 r.p.m.) for 16 h, filtered and the supernatant analysed for P colorimetrically (The Non-Affiliated Soil Analysis Work Committee, 1990).

4.2.2 Results and discussion

4.2.2.1 Chemical and physical characteristics

The tailings material was alkaline and the EC (Table 4.1) was within the ranges reported for other Pb/Zn mine tailings (Table 3.1). The pH<sub>KCl</sub> was higher than the pH<sub>water</sub>, attributed to the displacement of base cations from the PT in the salt-buffered solution. The OC content was also within the range reported for other Pb/Zn mine tailings (Table 3.1). Plant available nutrients (N and P), extractable base cations and CEC were low (Table 4.1). The tailings material had an appreciable CCE (Table 4.1), which was attributed to the presence of carbonate minerals, notably dolomite (Section 4.2.2.5).

**Table 4.1** Basic chemical characteristics of the Pering Mine tailings material (PT)

Parameter		PT
pH	H <sub>2</sub> O	8.20
	1 M KCl	8.55
Electrical conductivity (25 °C)	(mS m <sup>-1</sup> )	51.5
Organic carbon	(g 100g <sup>-1</sup> )	0.44
AMBIC P	(mg kg <sup>-1</sup> )	2.03
NH <sub>4</sub> <sup>+</sup> -N	(mg kg <sup>-1</sup> )	6.78
NO <sub>3</sub> <sup>-</sup> -N	(mg kg <sup>-1</sup> )	2.37
Total N	(mg kg <sup>-1</sup> )	256
Extractable base cations (cmol <sub>c</sub> kg <sup>-1</sup> )	Ca	4.00
	Mg	1.75
	Na	0.04
	K	0.02
Cation exchange capacity	(cmol <sub>c</sub> kg <sup>-1</sup> )	2.26
Calcium carbonate equivalence	(%)	56.4
bd	below detection.	

The PT was found to consist of predominantly fine sand and silt, with low clay content (Table 4.2). The high amount of fine sand may lead to compaction problems (Skopp, 2000), reflected in the high bulk density (Table 4.2). Particle density was slightly higher (Table 4.2) than the generally accepted value of 2.65 g cm<sup>-3</sup> for a mineral soil (Skopp, 2000).

**Table 4.2** Basic physical properties of the Pering Mine tailings material (PT)

Parameter	PT
Particle density (g cm <sup>-3</sup> )	2.88
Bulk density (g cm <sup>-3</sup> )	1.75
Particle size (%)	
Coarse sand (0.50 – 2 mm)	0.05
Medium sand (0.25 – 0.5 mm)	5.35
Fine sand (0.053 – 0.25 mm)	79.4
Silt (0.002 – 0.053 mm)	13.4
Clay (<0.002 mm)	1.88

4.2.2.2 Saturated paste extracts

Saturated paste extractable metals (Table 4.3) in the PT were negligible in most instances indicating that they either exist primarily as insoluble phases in the material, probably as sulphides (Clevenger, 1990), or have been immobilised due to the elevated pH of the PT (Adriano, 1986; McBride, 1994; Gray *et al.*, 1998). Kabata-Pendias (2001) indicates that at neutral to alkaline pH, metal solubility is reduced due to precipitation as hydroxides, phosphates or carbonates and may also promote the formation of stable metal-organic complexes. Zhang *et al.* (2003) investigated the characteristics of metals from Pb/Zn mine tailings, in an area rich in carbonate, using a sequential fractionation procedure. They found that Pb was primarily associated with carbonate and oxide fractions; Cu and Zn with sulphide and organic fractions. They concluded that carbonate minerals play a role in mitigating movement of soluble forms of these metals. Concentrations of Ca, Mg and S were slightly elevated. The EC of the paste was high (356 mS m<sup>-1</sup>), nearing the 400 mS m<sup>-1</sup> value set for saline soils (United States Salinity Laboratory Staff, 1954). Conesa *et al.* (2006) report saturated paste EC values from 200 to 3 600 mS m<sup>-1</sup> (Table 3.1), indicating that elevated EC values are typical of tailings material. The sodium adsorption ratio of the PT was low (Table 4.3), indicating the Na was not the cause of the salinity. The high

concentration of soluble S, probably as soluble sulphate salts, was suspected to be the cause of the high EC.

**Table 4.3** Element concentrations in the saturated paste extract of tailings material from Pering Mine

Soluble elements (mg L <sup>-1</sup> )					
Al	Cd	Cr	Cu	Fe	
bd	bd	bd	0.04	bd	
Mn	Ni	Pb	S	Zn	
0.92	0.60	bd	915	1.73	
Base cations (cmol <sub>c</sub> L <sup>-1</sup> )				SAR	SP (%)
Ca	Mg	Na	K		
2.59	2.81	0.12	0.07	0.07	23.1

bd below detection.  
SAR sodium adsorption ratio ( $[\text{Na}^+]/[\text{Ca}^{2+} + \text{Mg}^{2+}]^{1/2}$ ).  
SP saturation percentage.

4.2.2.3 *Total elements*

The high concentrations of total Ca and Mg in both sample 1 and 2 (Appendix 4.2) reflect the dolomitic mineralogy of the PT (Section 4.2.2.5). This was also reflected in the high loss on ignition (XRF) values for the tailings, due to the loss of carbonate as CO<sub>2</sub> (Appendix 4.2). Total Zn concentrations were the highest of the trace metals. It was suspected that the differences were due to the occurrence of localised crystals of ZnS in the PT (see Section 4.2.2.5) that may have resulted in the variability in samples. Total Pb was considerably lower than the Zn concentrations, probably due to the lower initial amounts in the ore and effective Pb recovery during ore processing. The high total S concentration was attributed to the presence of sulphate salts and residual sulphide minerals. This was corroborated by XRD and EDX (Section 4.2.2.5).

4.2.2.4 *Extractable metals*

The DTPA extraction method was developed to estimate the amount of plant available metal (Cu, Fe, Mn and Zn) in neutral and calcareous soils (Lindsay and Norvell, 1978), but was used here for additional metals (Table 4.4). The concentrations of Pb and Zn were high compared to the other metals measured and tended to be higher than typical metal concentrations measured as the baseline levels of South African surface soils (Herselman

*et al.*, 2005) (Table 4.4). While the differences in methods do not allow for direct comparisons, the data show that only Zn was above the typical concentrations for “natural” soils. In some instances (Cd, Cu and Pb) the metal concentrations exceeded the mean value of the soils, but were well within the ranges reported for those metals. The concentrations of Pb, Cu and Cd found in the PT are, however, similar to metal concentrations reported for other Pb/Zn mine tailings, though the DTPA-extractable Zn concentration reported here is higher (Table 3.2).

**Table 4.4** Diethylenetriaminepentaacetic acid (DTPA)-extractable metal concentrations in the tailings from Pering Mine and ethylenediaminetetraacetic acid (EDTA)-extractable metal concentrations of surface soils in South Africa

Sample		Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
		----- (mg kg <sup>-1</sup> ) -----							
	Tailings	0.31	bd	6.00	2.60	4.08	0.14	37.6	957
South African surface soils <sup>†</sup>	Mean (n > 4300)	0.02	0.16	2.87	nd	nd	2.39	3.32	1.66
	Minimum	bd	bd	bd	nd	nd	bd	0.02	bd
	Maximum	1.46	12.5	67.3	nd	nd	170	109	210

† Herselman *et al.* (2005).  
 bd below detection.  
 nd not determined.

The TCLP solution extracted greater amounts of almost all metals compared to the acid rain extraction. This was attributed to the lower pH and metal complexing ability (acetic acid) of the TCLP solution (Table 4.5). The TCLP solution extracted high amounts of Zn and Mn, while the Pb concentration was also elevated. The lower amounts extracted by the acid rain are probably due to the high buffering capacity of the PT, this reflected in the neutral pH of the residual solution (Table 4.5), and the lower metal complexing ability of the carbonic acid solution.

Concentrations of TCLP-extractable Mn, Pb and Zn exceeded both the “acceptable environmental exposure” (AEE) and “acceptable human health exposure” (AHHE) limits (DWAF, 2005), while Cu exceeded only the AEE limit (Table 4.5). The AEE indicates the LC<sub>50</sub> x 0.1 of a contaminant that will lead to a mortality rate of one in three hundred thousand of an organism in an aquatic environment. The AHHE is the acceptable exposure limit of a contaminant, in water, for human health. It is calculated from the ‘reference dose’ or ‘tolerance daily intake’ derived from chronic toxicity studies and a 70 kg person

drinking 2 L of water a day (DWAF, 2005). The TCLP extraction was developed to mimic organic leachate from landfill conditions and is an unlikely scenario at this site. However, the TCLP extraction may offer some insight into the effect of plant root exudates on metal mobility in the PT, and thus implications for metal translocation into aerial plant parts or enhanced metal leaching to groundwater. When considered in terms of plant growth, the effects of roots would be greatest in the upper substrate layers. Metals mobilised in these regions are likely to be taken up by the plants or immobilised deeper in the tailings profile due to the high pH.

**Table 4.5** Final pH and concentrations of metals in the tailings from Pering Mine extracted with TCLP and acid rain solutions. The AEE<sup>†</sup> and AHHE<sup>‡</sup> are included for comparative purposes

Extract	Final pH	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
		----- (mg L <sup>-1</sup> ) -----							
TCLP	5.11	bd	bd	1.00	5.45	59.9	0.06	12.5	93.6
Acid rain	7.00	0.13	bd	bd	0.04	1.18	0.03	0.19	26.9
AEE		0.03	4.70	0.13	9	0.30	0.75 <sup>¶</sup>	0.12	0.83
AHHE		0.04	-	2.30	-	4.90	0.18 <sup>¶</sup>	0.02	11.0

bd below detection.  
† Acceptable environmental exposure (DWAF, 2005).  
‡ Acceptable human health exposure (DWAF, 2005).  
¶ Soluble nickel salts (DWAF, 2005).

In this instance the acid rain extraction may better reflect the potential toxicity of the waste under leaching conditions, as this method was developed to mimic acid produced when CO<sub>2</sub> dissolves in rainwater to produce acid rain (DWAF, 2005). Cadmium, Mn and Zn concentrations exceeded the AEE limits substantially, while Pb concentrations were only slightly higher than the AEE limit (Table 4.5). Only Cd, Pb and Zn concentrations were above the AHHE limit.

4.2.2.5 Mineralogy

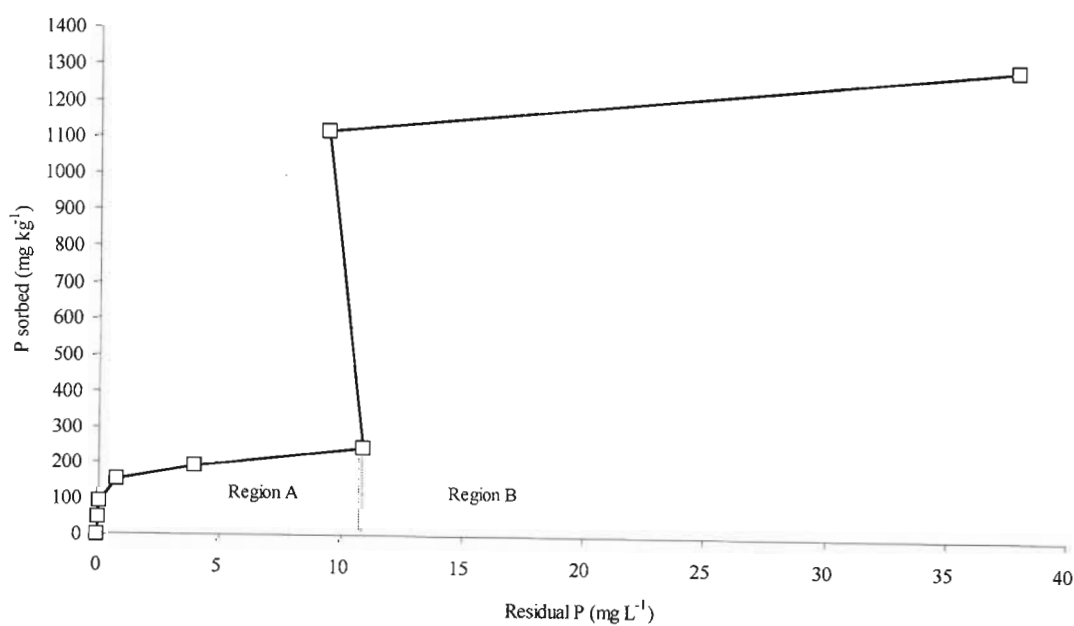
Scanning electron microscopy revealed that the PT was predominantly fine-grained (Appendix 4.3), with particles typically being less than 500 µm in length. This is reflected in the low amounts of coarse sand (> 500 µm) determined in the particle size analysis (Table 4.2). Qualitative determination of elemental composition by EDX showed that the

PT was predominantly Ca and Mg, with minor amounts of Al, K, Fe, Mn, S, Si and Zn. In some localised areas high amounts of Zn and S, and Fe and S were detected, reflecting the presence of the sulphide mineral forms (Appendix 4.3).

The XRD analysis indicates that the PT was crystalline with little amorphous constituents present. It consisted predominantly of dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), with minor amounts of quartz ( $\text{SiO}_2$ ), K-feldspar ( $\text{KAlSi}_3\text{O}_8$ ), sphalerite ( $\text{ZnS}$ ) and pyrite ( $\text{FeS}_2$ ). No traces of galena ( $\text{PbS}$ ) were evident.

4.2.2.6      *Phosphorus sorption*

A P sorption investigation was included as it was expected that the high pH and dolomitic mineralogy of the PT would lead to high P fixation. Assessing the extent of this may indicate the P requirements for adequate plant growth. Phosphorus sorption by the PT was described as an L-type curve (Sparks, 2003) at low adsorbate concentrations (Figure 4.1, Region A).



**Figure 4.1**      Phosphorus sorption isotherm for tailings from Pering Mine.

At low P solution concentrations, both the Langmuir and Freundlich models (Travis and Etnier, 1981) described the P sorption data well ( $R^2 = 0.991$  and  $0.988$ , respectively). The calculated maximum sorption ( $250 \text{ mg kg}^{-1}$ ), calculated from the linear form of the

Langmuir model, agrees well with the observed value of 247 mg kg<sup>-1</sup> taken from Figure 4.1, at a residual P concentration of about 11 mg L<sup>-1</sup>. However, at residual P concentrations greater than 11 mg L<sup>-1</sup> there was a sharp increase in P sorption (Figure 4.1, Region B), indicating that other processes, such as precipitation, may be occurring (Kuo and Lotse, 1972; Zhou and Li, 2001).

The amount of P sorbed to achieve residual P concentrations of 0.05 and 0.20 mg L<sup>-1</sup> was estimated from Figure 4.1 and also calculated using the linear form of the Langmuir model (Table 4.6). Residual solution P concentrations of 0.05 (Zupancic, 1996) and 0.20 mg L<sup>-1</sup> (Fox and Kamprath, 1970) are reported as soil solution P concentrations that will supply adequate P for plant growth. The calculated amount of P sorbed agrees well with the observed value at a residual P concentration of 0.20 mg L<sup>-1</sup>. However, at a residual concentration of 0.05 mg L<sup>-1</sup> the calculated value is 38% lower than the observed concentration. These data suggest that high amounts of additional P fertiliser will be required to achieve satisfactory plant growth.

**Table 4.6** The amount of P sorbed by Pering mine tailings to achieve residual P concentrations of 0.05 and 0.20 mg L<sup>-1</sup>. The ‘estimated’ value was extracted from the isotherm plot (Figure 4.1), and the ‘calculated’ value was determined using the linear form of the Langmuir isotherm

Determination	Amount of P sorbed (mg kg <sup>-1</sup> ) to achieve the residual P values (mg L <sup>-1</sup> ) indicated	
	0.05 <sup>†</sup>	0.20 <sup>‡</sup>
Estimated	50.5	102
Calculated	31.3	90.9

<sup>†</sup> Zupancic (1996).  
<sup>‡</sup> Fox and Kamprath (1970).

4.2.3 Conclusions

Apart from apparent macro-nutrient deficiencies, notably N and P, the PT has high concentrations of labile Zn (and to a lesser extent Pb) relative to “natural” soil concentrations (Herselman *et al.*, 2005). The high pH may inhibit plant growth and reduce nutrient availability. The high amount of fine sand may also lead to compaction problems, reflected in the high bulk density of the tailings. These are the primary factors that could hinder revegetation on the tailings material.

While the use of various amendments and ameliorants to improve the fertility, reduce metal availability and improve the physical properties of the tailings can be advocated, the use of these may be limited due to economic constraints. Common ameliorants such as composts, municipal sludges, and other industrial by-products are not readily available in the Pering Mine area, and the cost of importing such materials to use on the tailings dam would be prohibitively expensive. Use of commercially available supplemental fertiliser may alleviate some of the nutrient deficiencies, and can be readily obtained. However, high amounts of additional P may be necessary to counter the high sorption capacity of the tailings.

An alternative strategy is to use plants that have adapted to grow in adverse environments. These plants may include those that can tolerate unfavourable soil conditions, or are adapted to adverse climatic conditions. The following investigation examines the potential of selected grass species from the Pering Mine site and elsewhere as cover species for the tailings material.

### **4.3 The growth of selected grass species in tailings from Pering Mine**

#### **4.3.1 Introduction**

The use of indigenous plants to revegetate mine tailings is often more advantageous than using introduced or crop species (Kramer *et al.*, 2000). Indigenous plants may be better adapted to the environmental conditions at a site and require less maintenance. They also tend to be more tolerant of low nutrient levels and climatic stresses than agronomic crops, may provide long-term stability and be self-sustaining. These are favourable attributes as the costs associated with the sustained management of a revegetation programme may be substantially reduced. Furthermore, the use of native species is preferred as it removes any risks associated with invasive exotic species, while maintaining the integrity and biodiversity of the surrounding ecosystem.

The objectives of this investigation were to test the growth of five grass species common to the Pering Mine area, a grass species collected from an abandoned chrysotile tailings dam and a commercially available pasture grass frequently used for mine reclamation work.



The growth of these species was tested with different levels of inorganic fertiliser application under glasshouse conditions.

#### 4.3.2 Materials and methods

##### *4.3.2.1 Establishment of the pot experiment*

Pure tailings material was placed in a 1.9 L plastic pot (with a fine glass-wool membrane placed over the drainage-holes), lightly tapped a few times and the mass of material determined (3.3 kg). All pots were filled with this mass of tailings (by weighing) that approximated the field bulk density ( $1.7 \text{ g cm}^{-3}$ ). This bulk density was used for the calculation of fertiliser application rates, and, with the assumption of a 200 mm incorporation depth, a mass of 3 400 000 kg tailings material  $\text{ha}^{-1}$  was calculated. Fertility analysis indicated that the tailings material had negligible available N and P, with very low K (Section 4.2.2.1). In addition, the P sorption investigation found that the material had a very high P sorbing capacity (Section 4.2.2.6). Thus an initial basal fertiliser was applied to each pot consisting of the equivalent of 100 kg N, 150 kg P and 100 kg K  $\text{ha}^{-1}$ . As the material had a very alkaline pH, acidifying fertilisers (i.e.,  $\text{K}_2\text{SO}_4$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{NH}_4\text{NO}_3$ ) were used to make up the fertiliser solutions. To achieve the desired fertiliser levels 4.32 g  $\text{K}_2\text{SO}_4$ , 10.82 g  $\text{NH}_4\text{H}_2\text{PO}_4$  and 1.78 g  $\text{NH}_4\text{NO}_3$  were dissolved in 1 L of distilled water. A 50 mL aliquot was then diluted to 400 mL and used to water each pot. This level is referred to as the full fertiliser application rate. In addition, half this fertiliser rate (25 mL aliquot diluted to 400 mL) and unfertilised (400 mL water) were also used.

The species tested were *Andropogon eucomus* Nees, *Cenchrus ciliaris* L., *Cymbopogon plurinodis* Stapf ex Burt Davy, *Digitaria eriantha* Steud, *Eragrostis superba* Peyr, *Eragrostis tef* (Zucc.) Trotter and *Fingeruthia africana* Lehm. A brief description of each grass species is given in Appendix 4.4. Seed of *C. ciliaris*, *C. plurinodis*, *D. eriantha*, *E. superba* and *F. africana* were collected from the Pering Mine site, all growing near or on the tailings dam. These were the only species that had viable seed at the time of sampling (mid-February 2004). Seed of *A. eucomus* was collected from the tailings dam of an abandoned chrysotile asbestos mine (Stella Mine) near Barberton (eastern Mpumalanga,

South Africa). This species is reported to grow well under disturbed conditions (Dr. J.E. Granger<sup>1</sup>, *pers. comm.*), which were evident at the asbestos mine (Plate 4.2).



**Plate 4.2**     *Andropogon eucomus* growing on tailings from abandoned asbestos mine (Stella Mine) near Barberton, Mpumalanga.

A commercial variety of *E. tef* was tested, as this species is often used as a ‘nurse crop’ in mine revegetation operations to provide rapid soil cover and improve soil conditions for the establishment of more persistent species (Jones *et al.*, 1975; Wood and Buchanan, 2000).

Initial investigations found that germination of the collected seed was poor in the tailings material, and thus seed was germinated in seedling trays in commercially available seedling mix. Three seedlings were then transplanted into the tailings material. Only *E. tef* was seeded directly into the tailings material as this had high germination success. Unfortunately, germination of the *D. eriantha* seed was poor, so seed of a commercially available variety of *D. eriantha* was used. Fertiliser solutions were only added once the seedlings were planted, or in the case of *E. tef*, once the seeds had germinated, to avoid

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<sup>1</sup> Dr. J.E. Granger, Discipline of Range and Forage Resources, University of KwaZulu-Natal, Pietermaritzburg, South Africa.

‘fertiliser burn’. Although *E. tef* seed germinated well, seedlings did not survive for long, and so this species was excluded from the investigation. *Cenchrus ciliaris*, *D. eriantha* and *E. superba* grew well and were harvested six weeks after planting. The other species grew more slowly and had not reached suitable biomass for harvesting at six weeks and were left for an additional two weeks when all remaining species were harvested and the experiment terminated. Plants were harvested by cutting the above-ground foliage about 10 mm from the substrate surface.

#### 4.3.2.2 *Analysis of plant material*

The roots were removed from the tailings material and washed to remove surface-adhering tailings particles. Sample mass of above and below-ground biomass was determined after all material was dried in a forced-draft oven at 65 °C for 2 days. All plant material was milled in a mechanical mill, and the ground material collected and stored in 100 mL plastic vials. Plant samples were wet digested with concentrated nitric acid using the method adapted from Slatter (1998; Appendix 4.5).

Digests of *C. ciliaris*, *D. eriantha* and *E. superba* were analysed for Ca, Cu, Fe, K, Mg, Mn, Pb and Zn by AAS, and P was determined colorimetrically (The Non-Affiliated Soil Science Working Committee, 1991). Calcium, K, Mg and P were analysed to determine the major nutritional status of these grasses. Digests of the other grass species (and root material of all grass species) were only analysed for Cu, Fe, Mn, Pb and Zn. Due to poor yield of some grass species, plant material was bulked and analyses conducted in duplicate, negating the use of statistical comparisons in these instances. In all digestion batches (40 samples per batch) a reference ryegrass sample was analysed as a quality control sample. The ryegrass sample was supplied by the Department of Agriculture Analytical Services Division (Cedara), and is used as a quality control sample in their laboratories. Consistent results were found between the quality control sample analysed and analysis given by Cedara for the sample. A blank sample was also included in every batch.

#### 4.3.2.3 *Statistical analysis*

Overall differences between means of the yield of foliage and roots of the grass species were compared by analysis of variance (ANOVA), using the statistical package Genstat 8.1

(Lawes Agricultural Trust, Rothamsted Experimental Station, 2005). As there were differences in the growth periods of some of the species tested an additional variate (covariate) was used to account for these differences in the ANOVA (Rayner, 1967). Where the overall F-statistic for the grass by fertiliser level interaction was found to be significant, means were compared by LSD at the 5% level of significance (Genstat 8.1). Elemental concentrations of the foliage were not analysed in this manner due to lack of replication of some treatments. The correlation between yield (of foliage and roots) and fertiliser application rate were determined by linear regression analysis (Genstat 8.1).

### 4.3.3 Results and discussion

#### *4.3.3.1 Foliage yield*

As expected the yield of all grass species increased with an increase in fertiliser application rate (Table 4.7), though there was a significant ( $F_{10,34} = 3.62$ ;  $p = 0.002$ ) species by fertiliser interaction. The yield of *C. ciliaris* (Plate 4.3a) at the high fertilisation rate was higher ( $p < 0.05$ ) than all other grass species at any fertilisation level (Table 4.7). Similarly the yield of *D. eriantha* (Plate 4.3b) at the full fertilisation rate was higher ( $p < 0.05$ ) than all other treatments except for *C. ciliaris* at the full fertilisation rate. There were no differences ( $p > 0.05$ ) between the yield of *D. eriantha* and *C. ciliaris* at the half and zero fertiliser levels (Table 4.7). However, it should be noted that the variability in the yield of *D. eriantha* was high (Table 4.7).

*Cymbopogon plurinodis* had the third highest yield at all fertiliser levels, though it grew for eight weeks to achieve this biomass (Table 4.7). The yield of *E. superba* (Plate 4.3c) was similar to that of *F. africana* and *A. eucomus* had the lowest yield at all levels of fertilisation (Table 4.7). Generally strong linear correlations existed between the yield and fertiliser application rate except for *D. eriantha* (Table 4.8). This was attributed to the high variability between replicates of the yields of *D. eriantha* (Table 4.7).

The increase in yield with increasing fertiliser application was expected considering the low initial fertility of the PT (Section 4.2.2.1), suggesting that the use of inorganic fertiliser would be important when revegetating the tailings dam. Though the use of organic amendments was not investigated here it is likely that if these are used in conjunction with

inorganic amendments, improved yields are likely, improving sustainability in the long-term. Many authors have reported significantly higher yields of plant species when additional sources of organic matter were added to tailings material (e.g. Ye *et al.*, 1999; Shu *et al.*, 2002) due to improved chemical and physical conditions for plant growth.

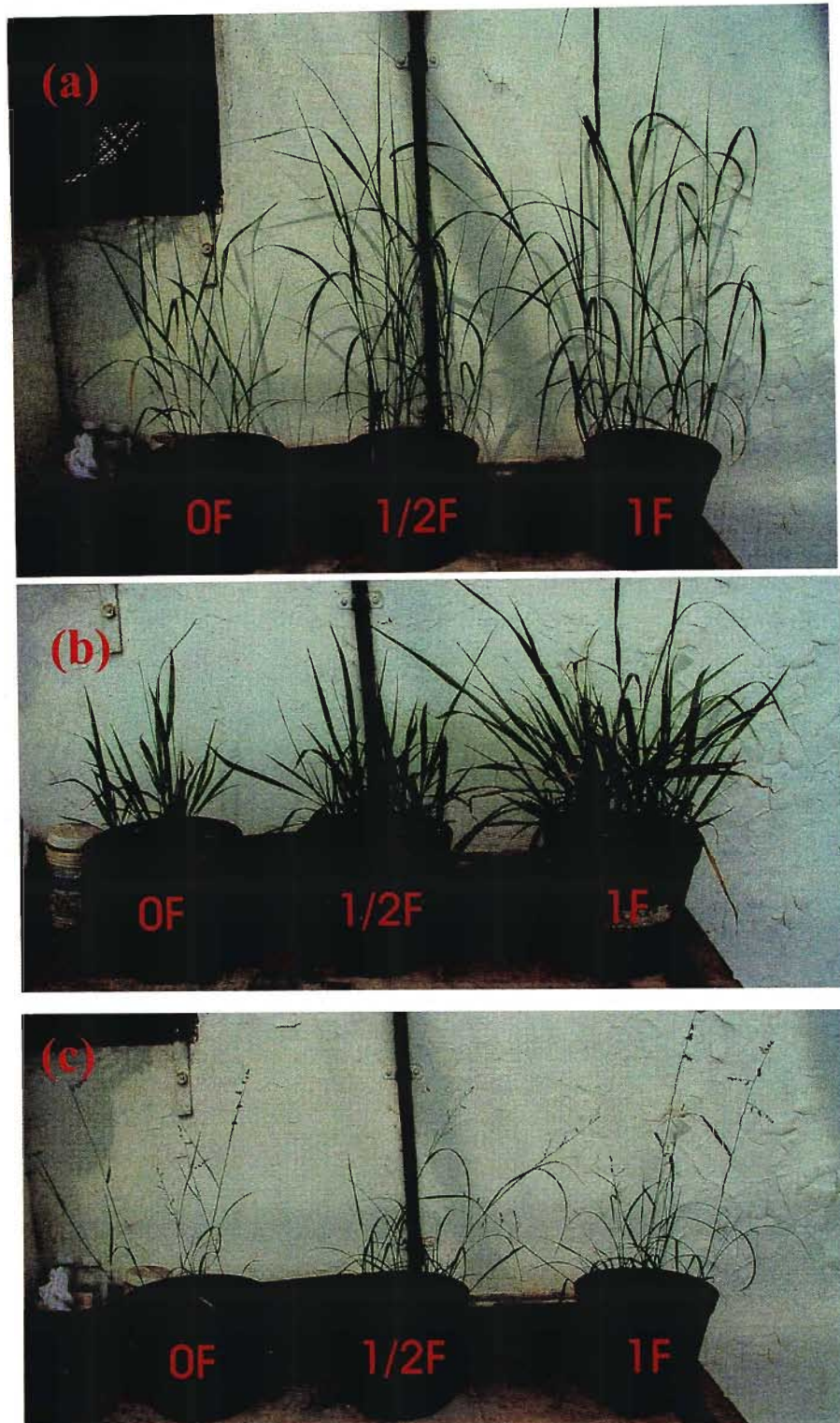
**Table 4.7** Mean yield ( $\pm$  SE,  $n = 3$ ) of foliage biomass for six grass species grown in tailings from Pering Mine at three levels of fertiliser

Grass species	Fertiliser level <sup>†</sup>	Leaf yield $\pm$ SE (g pot <sup>-1</sup> )
<i>Andropogon eucomus</i>	0	0.14 $\pm$ 0.06 k <sup>‡</sup>
	Half	0.70 $\pm$ 0.20 hij
	Full	0.91 $\pm$ 0.13 ghi
<i>Cenchrus ciliaris</i>	0	1.38 $\pm$ 0.04 efg
	Half	2.73 $\pm$ 0.10 cd
	Full	4.02 $\pm$ 0.25 a
<i>Cymbopogon plurinodis</i>	0	0.87 $\pm$ 0.13 ghij
	Half	1.66 $\pm$ 0.14 e
	Full	2.27 $\pm$ 0.28 d
<i>Digitaria eriantha</i>	0	1.50 $\pm$ 0.60 ef
	Half	2.68 $\pm$ 0.52 d
	Full	3.43 $\pm$ 0.86 b
<i>Eragrostis superba</i>	0	0.50 $\pm$ 0.12 ijk
	Half	1.05 $\pm$ 0.08 fgh
	Full	1.55 $\pm$ 0.18 ef
<i>Fingeruthia africana</i>	0	0.39 $\pm$ 0.12 jk
	Half	1.27 $\pm$ 0.34 efg
	Full	1.61 $\pm$ 0.07 e

<sup>†</sup> 0, half and full refer to the fertiliser application rate where full is the equivalent of 100 kg N, 150 kg P and 100 kg K ha<sup>-1</sup>, half is the equivalent of 50 kg N, 75 kg P and 50 kg K ha<sup>-1</sup>; and 0 was no fertiliser added.

<sup>‡</sup> Letters that are different indicate significant differences between means (LSD<sub>5%</sub>: leaf yield = 0.52; coefficient of variation = 4.7%).





**Plate 4.3** Growth (6 weeks) of (a) *Cenchrus ciliaris*, (b) *Digitaria eriantha* and (c) *Eragrostis superba* in tailings from Pering Mine treated with inorganic fertiliser where 0F (0 fertiliser), 1/2F (half fertiliser) and 1F (full fertiliser) refer to the fertiliser application rate where full is the equivalent of 100 kg N, 150 kg P and 100 kg K ha<sup>-1</sup>, half is the equivalent of 50 kg N, 75 kg P and 50 kg K ha<sup>-1</sup>; and 0 was no fertiliser added. Each pot is 190 mm in height.

**Table 4.8** Linear correlations between yield of grasses and fertiliser application rate, indicating significance of the linear correlation

Grass species	Linear correlation (Foliage biomass = )	R <sup>2</sup>
<i>Andropogon eucomus</i>	(0.08 x Fert <sup>†</sup> ) + 0.20***	0.81
<i>Cenchrus ciliaris</i>	(2.63 x Fert) + 1.40***	0.98
<i>Cymbopogon plurinodis</i>	(1.39 x Fert) + 0.90***	0.91
<i>Digitaria eriantha</i>	(1.93 x Fert) + 1.58**	0.62
<i>Eragrostis superba</i>	(1.05 x Fert) + 0.51***	0.93
<i>Fingeruthia africana</i>	(1.22 x Fert) + 0.48***	0.82

<sup>†</sup> Fertiliser application level (0, 0.5 or 1).  
\*\* and \*\*\* refer to level of significance with \*\* =  $p < 0.01$  and \*\*\* =  $p < 0.001$ .

4.3.3.2 Root yield

Similarly to the above-ground yield of the grasses, there was an increase in root biomass with increasing fertiliser application rate (Table 4.9), though the overall differences between means were not significant ( $F_{10,34} = 1.87$ ;  $p = 0.085$ ) for the fertiliser by grass interaction. *Digitaria eriantha* produced the highest root biomass at all fertiliser application levels (Table 4.9). Root biomass of *C. plurinodis* was second highest, but tended to be only marginally higher than the root biomass produced by *C. ciliaris* for each respective fertiliser level. Root biomass of *A. eucomus*, *E. superba* and *F. africana* were similar at each fertiliser level. Shu *et al.* (2002) also reported an increase in root biomass of four different grass species after fertiliser application.

Generally poor linear correlations existed between root yield and fertiliser application rate (Table 4.10). However, in all cases, the correlations were found to be significant (Table 4.10). The strongest correlation was recorded for *E. superba* ( $R^2 = 0.80$ ) and *C. ciliaris* ( $R^2 = 0.73$ ). *Andropogon eucomus* had the weakest correlation ( $R^2 = 0.37$ ) that was only marginally significant ( $p = 0.05$ ).

**Table 4.9** Mean yield ( $\pm$  SE,  $n = 3$ ) of root biomass of six grass species grown in tailings from Pering Mine at three levels of fertiliser

Grass species	Fertiliser level <sup>†</sup>	Root yield $\pm$ SE (g pot <sup>-1</sup> )
<i>Andropogon eucomus</i>	0	0.66 $\pm$ 0.14
	Half	1.59 $\pm$ 0.45
	Full	1.43 $\pm$ 0.14
<i>Cenchrus ciliaris</i>	0	1.42 $\pm$ 0.25
	Half	2.09 $\pm$ 0.38
	Full	2.88 $\pm$ 0.54
<i>Cymbopogon plurinodis</i>	0	1.78 $\pm$ 0.37
	Half	2.35 $\pm$ 0.38
	Full	2.94 $\pm$ 0.38
<i>Digitaria eriantha</i>	0	4.00 $\pm$ 1.26
	Half	5.45 $\pm$ 0.20
	Full	6.42 $\pm$ 0.44
<i>Eragrostis superba</i>	0	0.64 $\pm$ 0.27
	Half	1.38 $\pm$ 0.26
	Full	1.70 $\pm$ 0.04
<i>Fingeruthia africana</i>	0	0.71 $\pm$ 0.04
	Half	1.23 $\pm$ 0.39
	Full	1.37 $\pm$ 0.21

<sup>†</sup> 0, half and full refer to the fertiliser application rate where full is the equivalent of 100 kg N, 150 kg P and 100 kg K ha<sup>-1</sup>; half is the equivalent of 50 kg N, 75 kg P and 50 kg K ha<sup>-1</sup> and 0 was no fertiliser added. (coefficient of variation = 4.0%).

**Table 4.10** Linear correlations between root biomass of grasses and fertiliser application rate, indicating significance of the linear correlation

Grass species	Linear correlation (Root biomass = )	R <sup>2</sup>
<i>Andropogon eucomus</i>	(0.76 x Fert <sup>†</sup> ) + 0.85*	0.37
<i>Cenchrus ciliaris</i>	(1.46 x Fert) + 1.40**	0.73
<i>Cymbopogon plurinodis</i>	(1.16 x Fert) + 1.78**	0.66
<i>Digitaria eriantha</i>	(2.42 x Fert) + 4.08**	0.66
<i>Eragrostis superba</i>	(1.06 x Fert) + 0.71***	0.80
<i>Fingeruthia africana</i>	(0.66 x Fert) + 0.77**	0.53

<sup>†</sup> Fertiliser application level at either 0, half or full where full refers to the fertiliser application rate where full is the equivalent of 100 kg N, 150 kg P and 100 kg K ha<sup>-1</sup>; half is the equivalent of 50 kg N, 75 kg P and 50 kg K ha<sup>-1</sup>; and 0 was no fertiliser added.

\*, \*\*, \*\*\* refer to level of significance with \* =  $p < 0.05$ ; \*\* =  $p < 0.01$  and \*\*\* =  $p < 0.001$ .



#### 4.3.3.3 *Element uptake*

The Ca and Mg concentrations of *C. ciliaris* were lower than that of *D. eriantha* and *E. superba*, which had similar concentrations to each other (Table 4.11). The K concentrations were similar between all the grass species in the fertilised treatments, but higher in *C. ciliaris* in the control treatment. The K concentrations of *C. ciliaris* decreased with an increase in fertiliser application rate, while the reverse was true for the other two grass species (Table 4.11). The P concentrations were lowest in *C. ciliaris* and *D. eriantha*, but only *D. eriantha* exhibited purpling of the leaves (Plate 4.4), a typical symptom of P deficiency.

Concentrations of Ca, Mg and K were within acceptable ranges and P concentrations were generally below the adequacy range reported for grasses (Table 4.11). In the case of *E. superba*, P concentrations were similar to the adequacy values reported for turfgrass (Bennett, 1993). The low initial P concentration of the PT and its high P sorption capacity (Section 4.2.2.6) may have led to low P uptake by *C. ciliaris* and *D. eriantha*, while the high yield of these two species may have created a dilution effect. While N was not determined on the samples, N deficiencies were suspected from the yellowing of leaves of *D. eriantha* and *C. ciliaris*, but not *E. superba*. It is possible that the high biomass of both *D. eriantha* and *C. ciliaris* led to the deficiencies in N and P observed due to higher demand for these nutrients by the plants and a dilution effect. *Eragrostis superba* may also be better adapted to nutrient stress, considering it is adapted to grow at disturbed sites (Appendix 4.4).

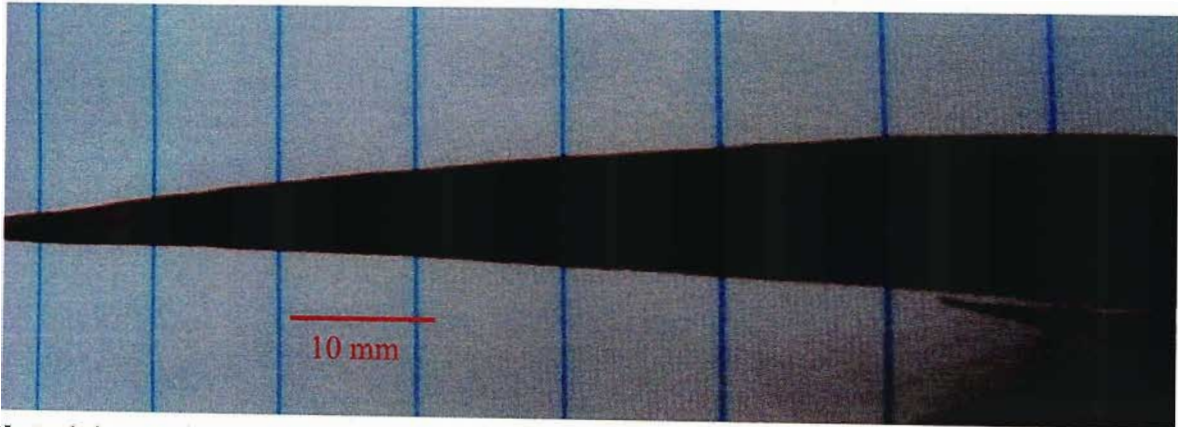
There were no clear trends in Cu uptake by any of the grasses with respect to fertiliser application (Table 4.12). In some instances (*C. ciliaris*, *C. plurinodis*, *D. eriantha* and *E. superba*), Cu concentrations increased with increasing fertiliser application. Furthermore, some treatments had very high variability (e.g. *C. ciliaris* at the half fertiliser level). Iron uptake was also variable with no consistent pattern evident for any of the grass species, with high variability between replicates of some treatments. The high Fe concentration reported for *A. eucomus* at the full fertiliser application rate was attributed to an anomalous reading obtained for one of the sample replicates that skewed the data. Unfortunately, due to limited sample size, this could not be repeated. Disregarding the anomalous replicate ( $366 \text{ mg kg}^{-1}$ ), a value of  $49.8 \text{ mg kg}^{-1}$  is obtained. This is more likely in the light of other

values obtained for this and other species. Nonetheless, concentrations of both Cu and Fe were generally within the typical range reported for turfgrass (Table 4.12). *Fingeruthia africana* was the only species that had Fe concentrations well below the recommended sufficiency range (Table 4.12), possibly resulting in the low yield of this species.

**Table 4.11** Concentrations of Ca, K, Mg and P in the foliage of three grass species grown in Pering Mine tailings at three levels of fertiliser application. The adequacy ranges for essential plant nutrients are reported for ‘turfgrass’ (Bennett, 1993) and for other selected grass species (Miles, 1994)

Grass species	Fertiliser rate <sup>†</sup>	Mg	Ca	K	P
		(%)			
<i>Cenchrus ciliaris</i>	0	0.17	0.24	2.25	0.04
	Half	0.18	0.26	2.17	0.10
	Full	0.22	0.25	2.10	0.03
<i>Digitaria eriantha</i>	0	0.45	0.54	1.73	0.09
	Half	0.37	0.41	2.14	0.05
	Full	0.38	0.44	2.23	0.09
<i>Eragrostis superba</i>	0	0.34	0.53	1.87	0.21
	Half	0.32	0.56	1.99	0.13
	Full	0.32	0.47	2.79	0.14
Bennett (1993)	‘turfgrass’	0.20–0.60	0.50–1.20	1.00–2.50	0.10–0.40
Miles (1994)	<i>Eragrostis curvula</i>	0.07–0.14	0.22–0.31	0.90–1.60	0.16–0.21
	<i>Festuca arundinacea</i>	0.20–0.36	0.10–0.25	2.20–3.50	0.25–0.35

<sup>†</sup> 0, half and full refer to the fertiliser application rate where full is the equivalent of 100 kg N, 150 kg P and 100 kg K ha<sup>-1</sup>; half is the equivalent of 50 kg N, 75 kg P and 50 kg K ha<sup>-1</sup>; and 0 was no fertiliser added.



**Plate 4.4** Apparent phosphorus deficiency observed in *Digitaria eriantha* grown in tailings from Pering Mine.

**Table 4.12** Mean concentrations<sup>†</sup> ( $\pm$  SE;  $n = 3$ ) of Cu, Fe, Mn, Zn and Pb in the foliage of six grass species grown in Pering Mine tailings at three levels of fertiliser application. The adequacy ranges for some essential plant metals are reported for 'turfgrass' (Bennett, 1993) and 'normal' and 'contaminated' ranges of metals are reported for plants (Ross, 1994)

Grass species	Fertiliser rate <sup>‡</sup>	Cu	Fe	Mn	Zn	Pb
		-----( $\text{mg kg}^{-1}$ )-----				
<i>Andropogon eucomus</i>	0	6.16	34.7	75.7	78.0	19.1
	Half	13.1 $\pm$ 4.8	54.8 $\pm$ 22.7	111 $\pm$ 29	430 $\pm$ 16	2.28 $\pm$ 1.21
	Full	9.71 $\pm$ 1.28	207 $\pm$ 223	170 $\pm$ 19	611 $\pm$ 131	1.22 $\pm$ 0.88
<i>Cenchrus ciliaris</i>	0	5.69 $\pm$ 0.37	75.8 $\pm$ 1.9	32.5 $\pm$ 5.5	167 $\pm$ 12	bd
	Half	6.47 $\pm$ 13.40	31.5 $\pm$ 10.1	34.5 $\pm$ 4.5	277 $\pm$ 31	2.16 $\pm$ 0.58
	Full	6.96 $\pm$ 0.31	55.0 $\pm$ 8.5	49.7 $\pm$ 17.7	381 $\pm$ 33	7.46 $\pm$ 2.41
<i>C. plurinodis</i>	0	6.62 $\pm$ 031	53.8 $\pm$ 3.9	37.4 $\pm$ 6.8	56.7 $\pm$ 41.4	4.20 $\pm$ 0.96
	Half	7.94 $\pm$ 1.27	54.4 $\pm$ 1.8	51.3 $\pm$ 4.6	336 $\pm$ 89	1.82 $\pm$ 0.91
	Full	9.08 $\pm$ 0.47	55.5 $\pm$ 2.7	64.1 $\pm$ 3.9	621 $\pm$ 48	1.60 $\pm$ 0.66
<i>Digitaria eriantha</i>	0	6.56 $\pm$ 0.58	69.1 $\pm$ 6.9	88.9 $\pm$ 19.0	312 $\pm$ 12	11.6 $\pm$ 3.97
	Half	7.55 $\pm$ 1.34	69.5 $\pm$ 29.2	112 $\pm$ 18.4	562 $\pm$ 192	6.41 $\pm$ 6.81
	Full	10.2 $\pm$ 0.6	88.6 $\pm$ 9.5	126 $\pm$ 30	918 $\pm$ 112	1.49 $\pm$ 1.29
<i>Eragrostis superba</i>	0	5.98	54.7	44.6	564	5.22
	Half	7.63 $\pm$ 0.64	60.7 $\pm$ 7.4	83.4 $\pm$ 7.4	989 $\pm$ 136	9.50 $\pm$ 1.98
	Full	8.84 $\pm$ 0.36	75.8 $\pm$ 8.4	117 $\pm$ 8	1105 $\pm$ 92	13.1 $\pm$ 2.94
<i>Fingerruthia africana</i>	0	11.7 $\pm$ 3.5	24.9 $\pm$ 1.2	31.8 $\pm$ 1.2	348 $\pm$ 20	9.71 $\pm$ 1.51
	Half	10.8 $\pm$ 0.7	27.5 $\pm$ 0.7	31.2 $\pm$ 1.8	576 $\pm$ 136	2.54 $\pm$ 0.33
	Full	13.1 $\pm$ 0.2	28.3 $\pm$ 0.8	41.2 $\pm$ 0.5	1153 $\pm$ 74	2.06 $\pm$ 0.86
Bennett (1993)		5-20	35-100	25-150	22-30	-
Ross (1994)	'Normal'	4-15	-	15-1000	8-400	0.1-10
	'Contaminated'	20-100	-	300-500	100-400	30-300

<sup>†</sup> Due to low yield not all three replicates could be analysed, thus replicates were bulked and analysed in duplicate. The control treatments of *A. eucomus* and *E. superba* only had a single analysis so the standard deviation from the mean could not be calculated.

<sup>‡</sup> 0, half and full refer to the fertiliser application rate where full is the equivalent of 100 kg N, 150 kg P and 100 kg K ha<sup>-1</sup>; half is the equivalent of 50 kg N, 75 kg P and 50 kg K ha<sup>-1</sup>; and 0 was no fertiliser added.

bd below detection.

For all grass species, except *F. africana*, there was an increase in Mn uptake with increasing fertiliser applications. In the case of *F. africana* at the full fertiliser application rate, Mn concentration of the foliage was higher (41.2 mg kg<sup>-1</sup>) than at the half and 0

fertiliser application rates, which were similar (31.8 and 31.2 mg kg<sup>-1</sup>, respectively). Uptake between the grass species was also highly variable. *Cymbopogon plurinodis* and *F. africana* accumulated markedly less Mn than the other species. As with Cu and Fe, the Mn concentrations were within the adequacy range reported for turfgrass and plants (Table 4.12).

Zinc concentrations varied markedly between grass species, though there were marked increases in Zn concentrations (two to eleven-fold) with increasing fertiliser applications for all species. Zinc concentrations of grass species and treatments were typically over the adequacy range reported for turfgrass (Table 4.12) and in *E. superba* and *F. africana*, the concentrations exceeded 1000 mg kg<sup>-1</sup> at the full fertiliser application rates. Excess Zn can lead to toxicity resulting in stunted root and shoot growth and chlorosis of new leaves (Farago, 1994; Kabata-Pendias, 2001). The upper range for Zn toxicity in plants is reported to be from 100 to 500 mg kg<sup>-1</sup>, and most plant species show a high tolerance to high Zn concentrations (Kabata-Pendias, 2001). The high Zn concentrations may have contributed to sub-optimal yields, though no visual symptoms of toxicity were evident. The elevated Zn concentrations of the foliage were attributed to the high amounts of labile Zn in the PT. The increase in Zn concentrations (and to some extent Mn) with increasing fertiliser application may have been due to the acidifying effect of the fertiliser and roots in the tailings material. It was shown that root yield increased with an increase in fertiliser application, compounding the acidifying effects that roots may have had, especially in the rhizosphere zones.

Lead concentrations were variable among the grass species, the highest uptake measured in the control treatment of *A. eucomus* (19.1 mg kg<sup>-1</sup>), though this was based on an unreplicated analysis. For *C. ciliaris* and *E. superba*, Pb uptake increased with increasing fertiliser application, while decreases were observed for the other grass species. Uptake of Pb by plants tends to be limited due to its relative immobility in the soil, though some organo-lead species are readily taken up by plants (Kabata-Pendias, 2001). Uptake of Pb by plants tends to be passive and it accumulates in the roots, where it is absorbed mainly by root hairs and stored in cell walls (Adriano, 1986; Kabata-Pendias, 2001). There is generally limited movement of Pb to aerial parts of plants (Farago, 1994). This suggests that the elevated concentrations of Pb in a soil do not necessarily lead to long-term forage contamination, which is supported by the findings of this investigation.

Ye *et al.* (1999) reported mean Zn and Pb concentrations of 454 and 40 mg kg<sup>-1</sup>, respectively, in the foliage of *A. elongatum* grown in pure tailings. Addition of fertiliser led to slight increases in the uptake of Zn and Pb (490 and 59 g kg<sup>-1</sup>, respectively). The addition of fertiliser had a similar effect on Zn concentrations in the grasses tested in this study, though in some instances the increases were substantially greater than reported by Ye *et al.* (1999). The same was not true for Pb concentrations, however, the response being more variable in the grasses investigated here. In all cases though, Pb concentrations were lower than those reported by Ye *et al.* (1999). The higher Zn uptake found here was likely due to higher amounts of available Zn (DTPA-extractable) in the PT (957 mg kg<sup>-1</sup>) compared to the tailings used by Ye *et al.* (1999; 41 mg kg<sup>-1</sup>). The reverse was true for Pb, where the PT had 38 mg kg<sup>-1</sup> DTPA-extractable Pb and the tailings used by Ye *et al.* (1999) had 154 mg Pb kg<sup>-1</sup>. Generally, trace metal concentrations decrease with an increase in soil pH (Gray *et al.*, 1998). The low availability of most of the metals was probably due to the high pH of the tailings that led to immobilisation of the elements. Generally, it is not expected that the metal concentrations of the grasses tested here would lead to toxicity in grazing animals. The elevated Zn concentrations are cause for concern though. Chaney (1983; cited by Ye *et al.*, 1999) has noted that excessive dietary Zn (300 to 1000 mg kg<sup>-1</sup>), Pb (30 mg kg<sup>-1</sup>), and Cd (0.5 mg kg<sup>-1</sup>) can be toxic to sheep and cattle.

Inconclusive results were determined for chemical analysis of root material, with a number of samples with very high metal concentrations, though these were apparently not related to grass species or fertiliser application rate. This was attributed to inadequate removal of very fine tailings particles adhering to the root surfaces. Although the roots appeared clean, once digested, fine sediment was evident in the digestion tubes. The tailings material introduced in this manner led to erroneous root metal concentrations, and as the degree of this contamination could not be accounted for, this aspect of the study was omitted.

#### 4.3.4 Conclusions

The selection of plant species that are tolerant of environmental conditions present at a site would alleviate some of the problems associated with establishing the vegetative cover. In this instance the selection of grass species occurring on the Pering Mine was considered favourable, as these species are adapted to the climatic conditions of the area. Furthermore, the soil in this area is also alkaline, thus it was expected that the plants would better

tolerate the alkaline nature of the tailings. The selection of *A. eucomus* offered a potential alternative as it was found to grow well on an alkaline serpentinitic/chrysotile tailings dam. Unfortunately growth of this species was poor, thus it is not recommended for use at Pering Mine.

The data collected for *C. ciliaris* and *D. eriantha* suggest that these two species would be suitable for revegetation at the Pering Mine site. Their high yield, growth rate and tolerance of the substrate conditions will allow a substantial cover to be established that may improve substrate conditions, as well as providing micro-climates suitable for the establishment of other species. Even when no fertiliser was used, these two species had higher yield than the other grass species tested. It is likely that when grown in a pot, the plants became root bound, possibly reducing yield. Under field conditions where root growth would be largely unrestricted, greater root biomass may be achieved, and nutrient deficiencies would be less problematic. The growth rate of *E. superba* was high, even though the biomass yield was not as high as some of the other species. This species established very easily and field evidence suggested that this species also had high seed producing potential. Most of the seed collected from the site was viable suggesting high propagation potential. This is a favourable trait for rapid revegetation of derelict sites.

While the other two species (*F. africana* and *C. plurinodis*) collected from the Pering Mine yielded higher foliage biomass than *E. superba*, their growth rates were lower. This was not deemed to be a favourable characteristic for the primary phases of revegetating the tailings dam. These species may be more suitable as long-term additions to improve species diversity. Both *F. africana* and *C. plurinodis* are considered to be highly unpalatable, and addition of these species may reduce the movement of grazing animals onto the tailings dam, reducing the risk of development of paths that may increase the erosion potential of the tailings dam.

The establishment of a grassy cover is expected to be the quickest and most cost-effective way to develop a vegetative cover on derelict wastes. In this instance, the use of an inorganic fertiliser proved beneficial to plant growth. Additional trace nutrient fertiliser may overcome low micro-nutrient concentrations (e.g. Cu), while higher amounts of N and P may further enhance plant establishment and sustainability. While the use of organic amendments is advocated for use on the tailings, there appears to be no readily available

source in the vicinity of the site, limiting this as an option. A possible consideration is cattle manure that could be supplied by local farmers, though it is not known if sufficient quantities would be available for this to be a viable proposition.

The use of some leguminous shrubs may also be beneficial for long-term nitrogen availability in the tailings. The establishment of woody vegetation may also offer long-term advantages and be beneficial to the revegetation of the tailings dam at Pering Mine. The greater rooting volumes of shrubs and trees may offer greater stability to a greater depth of tailings, whilst reducing leachate volumes through the tailings. This will reduce the potential for groundwater contamination. Furthermore, it would improve the aesthetic appearance of the tailings dam. While not the focus of this study, further investigations could consider some of the local tree species, notably *R. lancea*, *G. flava*, *T. camphoratus*, and some of the *Acacia sp.* common to the area.

#### **4.4 Chemically-enhanced phytoremediation of the Pering Mine tailings**

##### **4.4.1 Introduction**

While some of the species tested previously showed natural ability to accumulate high amounts of metal (notably Zn) in the above-ground foliage, none could be classed as metal-hyperaccumulators. Generally, lack of accumulation is considered a favourable attribute as it will restrict the amount of metal that enters the food-chain. However, in some instances there is interest in using plants to ‘clean’ contaminated soils or substrates, commonly referred to as phyto-extraction. Phyto-extraction is the process where plants are used to accumulate a pollutant in above-ground biomass so that it may be harvested. This material is then either disposed of or, in the case of some metals, recovered (*e.g.* Schnoor, 1997, 2002; Miller, 1996; Garbisu and Alkorta, 2001; Prasad and Freitas, 2003; Sas-Nowosielska, 2004; Ernst, 2005). It is almost certainly one of the most well researched technologies in the field of phytoremediation (Salt *et al.*, 1998) and a brief outline is presented below.

Phyto-extraction has received much attention as it is advocated as a cost-effective and environmentally friendly approach to ‘clean’ or ‘phytomine’ soils that are contaminated with, or contain high amounts of, metals and metalloids (Garbisu and Alkorta, 2001). The

research into this technology has focused on metals, as they tend to persist in the environment, whereas organic compounds tend to degrade over time. Most plants will take up certain metals for biological functions (e.g. Fe, Mn, Zn, Cu, Ca and Mg), but some have developed the ability to take up some of these essential metals, such as Mn and Zn, far in excess of biological requirements, while others can accumulate metals that have no known function in biological processes (e.g. Ni, Cd, Hg, Cr; Garbisu and Alkorta, 2001). It is this ability that has led to the suggested use of these plants to remediate soils contaminated with those elements. The primary purpose advocated for phyto-extraction is the remediation of metal-contaminated soils, but it has also been suggested that the technology could be used to extract or 'mine' soils that have natural concentrations of metals that do not warrant traditional mining practices, but that may be of some economic value (Robinson *et al.*, 1997a, b; Schnoor, 1997, 2002; Brooks *et al.*, 1998; Brooks and Robinson, 1998; Anderson *et al.*, 1999; Garbisu and Alkorta, 2001; Prasad and Freitas, 2003; Sas-Nowosielska *et al.*, 2004).

Phyto-extraction can occur naturally (by using adapted hyperaccumulator species – also known as continuous phyto-extraction) or by inducing metal uptake by plants (treating the soil with chelating agents - induced phyto-extraction) that would otherwise not take up significant amounts of metal (Salt *et al.*, 1998). There is also research into the development of transgenic plants that can be used for this purpose (Lasat, 2000; Eapen and D'Souza, 2005; Kramer, 2005).

The limitations of using natural hyperaccumulators has led to the suggestion that, in some instances, the addition of chemical amendments to a contaminated soil to mobilise metals for plant uptake is feasible (Romkens *et al.*, 2002; Schmidt, 2003; Alkorta *et al.*, 2004). The basic premise of this technology is that some metals are immobile under normal soil conditions (e.g. Pb; Alkorta *et al.*, 2004). By mobilising or solubilising them, plant uptake can be increased to hyperaccumulator levels or higher. Furthermore, certain metals (e.g. Pb) are not readily taken up by plants and this can be overcome by chelating these metals in bio-available forms. This has the advantage that naturally high-biomass, non-hyperaccumulating plants can be induced to extract large amounts of metal from the soil.

The most common synthetic organic chelating agent is probably EDTA, but others such as DTPA, CDTA (1,2-cyclohexylenedinitrilotetraacetic acid), HEDTA (hydroxyethylene-



diaminetriacetic acid) and organic acids (nitriloacetic acid, citric, humic, acetic and oxalic) have also been proposed and tested (Schmidt, 2003; Alkorta *et al.*, 2004). The ability of chelating agents to increase metal solubility and availability is based on their capacity to form water-soluble, metal-organic complexes that are readily taken up by plants (Salt *et al.*, 1998; Schmidt, 2003).

Much of the research has focused on Pb uptake and the use of chelating agents that have a high affinity for this metal (EDTA), though it has been shown that the technology might be successfully employed for other metals (Schmidt, 2003). Schmidt (2003) summarised the change in Pb uptake by different crop plants when treated with different chelating agents (Table 4.13). These results suggest that this technology has potential to induce extreme hyperaccumulation in some situations.

**Table 4.13** Lead concentrations in plants after the addition of different chelating agents (Schmidt, 2003)

Plant	Chelate added	Concentration of Pb in plant		Total soil Pb
		Without	With chelate	
	---(g kg <sup>-1</sup> )---	------(mg kg <sup>-1</sup> )-----		---(mg kg <sup>-1</sup> )---
Perennial French ryegrass	4 (EDTA)	96	24000	6750
Pea	2 (HEDTA)	90	10600	2450
Corn	2 (HEDTA)	60	10200	2450
Cabbage	0.9 (EDTA)	125	5010	10600
Sunflower	5.8 (CDTA)	67	5200	4000
Indian mustard	2.9 (EDTA)	313	5000	600
Redtop grass	5.8 (CDTA)	25	3000	4000
Corn	5.8 (CDTA)	36	2600	4000
Corn	0.44 (EDTA)	90	500	2500
Perennial ryegrass	1 (EDTA)	50	330	110
Cabbage	2.9 (EDTA)	3	90	1100

Unfortunately the use of this technology is not without drawbacks. Probably the greatest criticism of the use of chelating agents is the very fact that they mobilise metals. While this may enhance plant uptake it also creates the risk of metal migration, in particular, increased leaching to groundwater of soluble metal compounds (McGrath and Zhao, 2003). In addition, inducing the uptake of high amounts of metal by non-hyperaccumulating or tolerant plant species tends to lead to a loss in vigour and even death of the plant, once the chelating agent has been applied. The effects on soil fauna and flora have not been extensively investigated either, and it is possible that the addition of chelating agents may

impact negatively on soil quality (Romkens *et al.*, 2002). Other considerations are that, as with natural phyto-extraction, above-ground plant biomass must be removed from the site and dealt with in an appropriate manner.

The first pot experiment using the tailings from Pering Mine (Section 4.3) showed that metal accumulation in grass species grown in the tailings was generally low, and that none of the species were hyperaccumulators. This suggested that either these plants were able to exclude metals or that some of the metals were bound in unavailable forms. It was also apparent that low fertility was a major contributor to poor growth, notably N and P. Nonetheless, *D. eriantha*, *C. ciliaris* and *E. superba* were identified for use in further experiments as they grew moderately well in the fertilised tailings. These three species were tested for their chemically-enhanced, metal-extracting potential when grown in the PT with two different organic chelating agents (EDTA and DTPA).

#### 4.4.2 Materials and methods

Tailings material (1.5 kg) was placed in pots (0.9 L) and lightly tapped a few times to achieve a bulk density of  $1.7 \text{ g cm}^{-3}$ . As described in Section 4.3.2.1 this bulk density was used for the calculation of fertiliser application rates. To ensure good plant growth double the fertiliser rate used in the previous pot experiment was applied to the tailings to achieve the equivalent of 200 kg N, 300 kg P and 200 kg K  $\text{ha}^{-1}$ . As before, the use of acidifying fertilisers was preferred, thus  $\text{K}_2\text{SO}_4$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{NH}_4\text{NO}_3$  were used to make up the fertiliser solutions. To achieve the desired fertiliser level, 10.45 g  $\text{K}_2\text{SO}_4$ , 52.26 g  $\text{NH}_4\text{H}_2\text{PO}_4$  and 8.60 g  $\text{NH}_4\text{NO}_3$  were dissolved in 5L of distilled water. A 50 mL aliquot was diluted to 200 mL and used to water the pots. The drainage holes of the pots were covered with a fine glass-wool membrane to reduce loss of sediment from the pots.

The species tested were *D. eriantha*, *C. ciliaris* and *E. superba*. Seed was germinated in seedling trays in commercially available seedling mix and transplanted at about three weeks into the tailings material. As germination was variable for the three grasses tested each was planted depending on date of germination.

After six weeks growth in the PT, the organic chelating agents were added. They were surface applied to each pot at rates of 0.25, 0.5, 1 and 2 g (either EDTA or DTPA) kg<sup>-1</sup> of tailings material. The plants were then allowed to grow for an additional week before harvesting. Harvested plants were oven dried at 65 °C in a forced draft oven for two days. All plant material was milled in a mechanical mill, and the ground material collected and stored in 100 mL plastic vials. Plant samples were wet digested with concentrated nitric acid using an adaptation of the method of Slatter (1998, Appendix 4.5). All solutions were analysed for Pb, Zn and Cu by AAS. The effect of chelating agent treatment and grass species on the uptake of Cu, Pb and Zn were compared by ANOVA using the statistical package Genstat 8.1.

To assess the success of chemically-enhanced phyto-extraction of the PT the bioconcentration factor (BCF) and metal extraction ratio (MER) were calculated for each treatment. The BCF is defined as the ratio of metal concentration in plant foliage to metal concentration in the soil (McGrath and Zhao, 2003; Mertens *et al.*, 2005). The MER was proposed by Mertens *et al.* (2005) to also account for the plant biomass produced and volume of soil to be cleaned. The MER is calculated as a percentage using the following equation:

$$\text{MER} = (C_{\text{plant}} \times M_{\text{plant}} / C_{\text{soil}} \times M_{\text{rooted zone}}) \times 100 \dots \dots \dots \text{Eq. 4.1}$$

where C<sub>plant</sub> is the metal concentration in the plant foliage, M<sub>plant</sub> is the mass of harvested plant material (yield), C<sub>soil</sub> is the metal concentration in the soil volume and M<sub>rooted zone</sub> is the mass of soil volume to be cleaned. Both factors were calculated using total metal concentrations in the PT determined from the XRF data for sample 1(Appendix 4.2).

4.4.3 Results and discussion

There were no substantial increases in the uptake of Cu or Zn with increasing application rates of either EDTA or DTPA (Table 4.14). Lead uptake increased more markedly, but the concentrations were still not very high. In the case of Cu concentrations of the grasses, the interaction between chelating agent addition and grass species was only marginally significant (F<sub>16,51</sub> = 1.90, p = 0.042), while the overall effect of species was highly

significant ( $F_{2,51} = 35.52, p < 0.001$ ) and the effect of chelating agents was non-significant ( $F_{8,51} = 1.55, p = 0.164$ ).

**Table 4.14** Mean ( $\pm$  SE, n = 3) uptake of Cu, Pb and Zn of *Eragrostis superba*, *Cenchrus ciliaris* and *Digitaria eriantha* grown in tailings from Pering Mine treated with 0, 0.25, 0.5, 1, and 2 g kg<sup>-1</sup> of either ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA)

Species	Treatment	Rate (g kg <sup>-1</sup> )	Cu	Pb	Zn
			----- (mg kg <sup>-1</sup> ) -----		
<i>Cenchrus ciliaris</i>	Control	0	7.72±1.06	7.64±1.15	268±16
		0.25	7.17±1.15	6.27±0.74	314±48
	DTPA	0.5	5.96±0.54	5.30±0.80	300±11
		1	7.07±0.98	7.18±0.61	317±23
		2	8.87±0.60	9.95±2.01	393±15
	EDTA	0.25	6.96±0.71	5.18±1.73	321±33
		0.5	7.39±1.85	7.76±3.22	269±59
		1	7.36±1.78	9.17±2.52	344±24
		2	8.02±1.50	13.9±0.8	330±70
<i>Digitaria eriantha</i>	Control	0	9.28±0.34	6.28±1.25	371±35
		0.25	8.93±0.88	5.76±0.93	501±125
	DTPA	0.5	11.5±2.0	5.99±0.68	405±65
		1	10.4±1.3	7.67±1.30	444±87
		2	9.94±0.23	7.54±1.87	387±89
	EDTA	0.25	9.84±0.99	8.70±0.62	547±71
		0.5	9.52±0.23	7.80±1.70	443±223
		1	8.12±1.38	8.53±1.87	392±66
		2	10.2±1.2	13.2±1.8	470±60
<i>Eragrostis superba</i>	Control	0	6.57±0.32	7.26±2.57	444±40
		0.25	7.56±0.59	8.89±1.79	442±126
	DTPA	0.5	7.13±0.91	9.91±1.47	449±239
		1	8.17±1.44	12.1±1.1	483±44
		2	7.76±1.39	12.9±3.5	565±119
	EDTA	0.25	7.87±1.45	10.1±2.1	500±77
		0.5	7.57±0.78	10.4±3.5	478±58
		1	7.91±0.76	12.6±2.2	571±151
		2	9.00±0.94	20.4±4.9	547±78

For Pb and Zn, the interactive effect of chelating agent addition and grass species was non-significant ( $F_{16,51} = 1.49$ ,  $p = 0.14$  and  $F_{16,51} = 0.75$ ,  $p = 0.73$ , respectively). The individual effects of grass species and chelating agent addition on the uptake of Pb were highly significant ( $F_{2,51} = 32.93$ ,  $p < 0.001$  and  $F_{8,51} = 19.64$ ,  $p < 0.001$ , respectively). In the case of Zn uptake only the effect of grass species was highly significant ( $F_{2,51} = 25.98$ ,  $p < 0.001$ ).

The highest Cu concentration was measured in *D. eriantha* treated with  $0.5 \text{ g kg}^{-1}$  DTPA, while the lowest were measured in *C. ciliaris* also treated with  $0.5 \text{ g kg}^{-1}$  DTPA. Generally *D. eriantha* had the highest Cu concentrations of any treatment. It was found that regardless of species or chelating agent, only 0.36 to 0.68% of the total Cu in pots was removed in a single harvest, requiring between 190 and 630 harvests to remove all the Cu.

Lead concentrations increased with increasing applications rates of EDTA for all grass species. The same trend was evident in the case of DTPA addition but was less marked. *Eragrostis superba* had higher uptake of Pb than either of the other two species for any given treatment, except for the control treatment where the Pb concentrations of *C. ciliaris* were marginally higher. The Pb concentration of *E. superba* treated with  $2 \text{ g kg}^{-1}$  EDTA was markedly higher than that of the  $0.25$ ,  $0.5$  and  $1 \text{ g kg}^{-1}$  EDTA and control treatments. A similar situation existed for the DTPA treatments, where the  $1$  and  $2 \text{ g kg}^{-1}$  DTPA treatments were greater than any of the other DTPA treatments. The EDTA treatments were also higher than equivalent DTPA treatments. A similar situation was true for *C. ciliaris* and *D. eriantha*. Generally, differences between Pb concentrations of *D. eriantha* and *C. ciliaris* were not markedly different for each respective treatment. It was found that the relative amount of Pb extracted was negligible ( $< 0.02\%$ ), requiring between 4 800 and 20 200 harvests to remove all the Pb from the pots.

Zinc uptake was variable with regard to chelating agent addition. Foliage concentrations were generally high, reflecting the high Zn concentration in the tailings material. For all three species, the addition of either DTPA or EDTA increased Zn uptake over the untreated controls, especially at higher additions of chelating agents. However, for each individual species the highest addition of either DTPA or EDTA ( $2 \text{ g kg}^{-1}$ ) generally did not increase Zn uptake dramatically over the respective control treatments. As reflected in the statistical analysis, the effect of grass species was marked. *Eragrostis superba* tended

to take up higher amounts of Zn than either of the other grass species. However, uptake it was found that for all species, regardless of the type or amount of chelating agent,  $< 0.13\%$  Zn was removed in a single harvest, requiring between 1 400 and 3 600 harvests to remove all the Zn. This is clearly not a feasible option, even if the total Zn concentration of the PT is halved.

The BCF values for Cu were over 100% for almost all treatments and tended to increase for all grass species with respect to chelating agent addition (Table 4.15). Overall, *D. eriantha* had higher BCF values for Cu than the other grass species, for each respective treatment. The highest BCF value was for *D. eriantha* grown in tailings treated with  $0.5 \text{ g kg}^{-1}$  DTPA (which also had the highest Cu concentration). The Pb values were very low, with no distinct trends evident (Table 4.15). The only discernible pattern was that at the highest rate of either DTPA or EDTA ( $2 \text{ g kg}^{-1}$ ), for each grass species, the BCF values tended to be higher than for the other treatments. No trends in the BCF values of Zn were evident for *D. eriantha* or *C. ciliaris*.

The BCF values for *E. superba* increased with increasing rates of either EDTA or DTPA (Table 4.15). Overall, *E. superba* had higher BCF values for Zn than *D. eriantha*, which were higher than those of *C. ciliaris*. No trends in MER values for any of the metals were evident and were  $< 1\%$  in all cases (Table 4.15). Overall, *E. superba* had higher MER values than either *C. ciliaris* or *D. eriantha* for each respective treatment.

McGrath and Zhao (2003), Mertens *et al.* (2005) and Audet and Charest (2007) indicate that, for phyto-extraction (be it natural or induced) to be feasible, a BCF of over 100% is required. The BCF values for Cu were almost all over 100% suggesting that the grasses could be used for phyto-extraction. However, the increase in Cu concentrations, relative to the control treatments, were slight with respect to chelating agent addition and reflected that induced uptake was limited. This may be due to low initial Cu concentration in the tailings material. This suggests that the chelating agents had a very small effect in increasing available or mobile Cu and consequently plant uptake was not dramatically altered by these treatments. The low uptake of both Pb and Zn by the grasses, relative to their total concentrations in the PT, resulted in very low BCF values.

**Table 4.15** Bioconcentration factor (BCF) (%) and metal extraction ratio (MER) (%) for Cu, Pb, and Zn concentrations of *Eragrostis superba*, *Cenchrus ciliaris* and *Digitaria eriantha* foliage grown in tailings from Pering Mine treated with 0, 0.25, 0.5, 1, and 2 g kg<sup>-1</sup> of either ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA)

Species	Treatment	Rate (g kg <sup>-1</sup> )	Cu		Pb		Zn	
			BCF	MER	BCF	MER	BCF	MER
<i>Cenchrus ciliaris</i>	Control	0	124	0.23	2.46	< 0.01	12.3	0.02
	DTPA	0.25	116	0.19	2.02	< 0.01	14.4	0.02
		0.5	96	0.19	1.70	< 0.01	13.8	0.03
		1	114	0.21	2.31	< 0.01	14.6	0.03
		2	143	0.23	3.20	< 0.01	18.1	0.03
	EDTA	0.25	124	0.23	2.46	< 0.01	12.3	0.02
		0.5	112	0.20	1.67	< 0.01	14.8	0.03
		1	119	0.22	2.50	< 0.01	12.4	0.02
		2	119	0.23	2.95	< 0.01	15.9	0.03
<i>Digitaria eriantha</i>	Control	0	150	0.30	2.02	< 0.01	17.1	0.03
	DTPA	0.25	144	0.20	1.85	< 0.01	23.1	0.03
		0.5	186	0.26	1.92	< 0.01	18.7	0.03
		1	168	0.19	2.47	< 0.01	20.5	0.02
		2	160	0.22	2.42	< 0.01	17.8	0.02
	EDTA	0.25	159	0.20	2.80	< 0.01	25.2	0.03
		0.5	154	0.22	2.51	< 0.01	20.4	0.03
		1	131	0.16	2.74	< 0.01	18.1	0.02
		2	164	0.20	4.25	< 0.01	21.7	0.03
<i>Eragrostis superba</i>	Control	0	106	0.19	2.33	< 0.01	20.5	0.04
	DTPA	0.25	122	0.27	2.86	< 0.01	20.3	0.05
		0.5	115	0.23	3.18	< 0.01	20.7	0.04
		1	132	0.26	3.90	< 0.01	22.2	0.04
		2	125	0.24	4.14	< 0.01	26.1	0.05
	EDTA	0.25	127	0.29	3.23	< 0.01	23.0	0.05
		0.5	122	0.25	3.35	< 0.01	22.0	0.05
		1	128	0.28	4.05	< 0.01	26.3	0.06
		2	145	0.24	6.56	0.01	25.2	0.04

Yoon *et al.* (2006) reported on the natural (i.e. not chelate-induced) BCF values for Cu, Pb and Zn of 36 different plant species growing on a metal contaminated site in north Florida. The highest BCF reported for Cu, Pb and Zn was 160, 1100 and 260%, respectively; considerably higher than was found in this study. Yoon *et al.* (2006) do suggest that consideration be given to the relative amounts of metal in the soil when assessing the relative effectiveness of phyto-extraction. For instance, similar to this investigation, they reported that Cu concentrations in the soil they investigated were very low, and given that Cu is an essential plant nutrient (Adriano, 1986), uptake and translocation to aerial plant

parts is expected. This leads to high BCF values, which indicate that a plant may have potential to phyto-extract Cu from the soil, even though Cu concentrations of the foliage are “normal” and the soil is not contaminated.

Mertens *et al.* (2005) argued that the BCF values are inadequate to assess the overall extracting potential of a plant and developed the MER which is an estimate of the amount of metal that may be removed from a known volume of soil, reported as a percentage of metal removed. In this study, all the values were below 15%, suggesting that chemically-enhanced phytoremediation is not feasible in the PT. Allowance must be made for the fact that this was a pot experiment, and certain limitations to the applicability of either the BCF or MER are likely. Furthermore, these indices are based on the total concentration of metals in the PT, perhaps not a suitable measure of the ultimate remediation potential.

A number of reasons are possible for the apparent lack of success of chemically-enhanced metal extraction from the PT. While a number of studies show dramatic increases in metal uptake due to chelating agent addition, this was not observed here. Many of these studies use artificially contaminated soils. Wu *et al.* (2004) suggested that metal-spiked soils may result in the high performance of phyto-extraction, partially due to the higher availability of metals in spiked soils. However, they do concede that in sites where long-term metal contamination is present, chemically-induced phyto-extraction has been shown to be a promising remedial tool. This does suggest, though, that depending on the form of a metal, the ability of a chelating agent to extract a metal may be reduced.

Competition by Ca, Mg, and other metal cations, for the binding sites of the chelating agent may also have resulted in the reduced effectiveness of the EDTA and DTPA. As both EDTA and DTPA are non-specific chelating agents (Kim *et al.*, 2003), other cations may be preferentially bound. For instance, while the conditional stability constants of EDTA complexes of Pb, Cu and Zn are higher than those of Ca or Mg (Kim and Ong, 1999), under conditions where concentrations of Ca or Mg exceed those of Pb, Cu and Zn, EDTA complexes with these base cations may be preferentially formed (Kim *et al.*, 2003). Some authors have suggested that under calcareous conditions an excess of chelating agent may be needed to overcome competition of target metals with base cations (Manouchehri *et al.*, 2006). Considering that the PT was dolomitic, consisting predominantly of Ca and Mg, competition for binding sites of the added chelating agent was highly likely.



#### 4.4.4 Conclusions

While a number of authors report substantial increases in the uptake of certain metals after the addition of organic chelating agents (e.g. Table 4.14), this was not observed here. Any increases due to the addition of the chelating agents tended to be small and the ineffectiveness of the chelating agents is highlighted by the low relative removal rates and low BCF and MER values. The highest increase (relative to the control treatment) was noted for Pb uptake, where at the highest rates of chelating agent application, foliage concentrations were typically double those of the respective controls. However, even the chemically-enhanced concentrations of Pb were low in the grasses, suggesting that this technology is not feasible on the alkaline tailings material. Higher concentrations of Zn, relative to the concentrations that are reported for grasses, were found in all the grass species tested. This indicates that Zn availability in the tailings was high and that the grasses could readily take up the Zn. The inability of the chelating-agents to notably enhance Zn uptake suggests that the grasses would naturally accumulate these elevated levels of Zn, though it did not qualify the plants as Zn hyperaccumulators. Greater success may be achieved by using substantially higher concentrations of chelating agent, though there would be associated cost implications and increased risk of metal leaching. However, it is probably not necessary, or practical, to attempt to phyto-extract the tailings for purposes of remediation.

## **PART 2**

# **THE LAND DISPOSAL OF TWO MANGANESE-RICH PROCESSING WASTES**

## CHAPTER 5

### LAND DISPOSAL OF INDUSTRIAL WASTES

#### 5.1 Introduction

With the advent of the industrial revolution large amounts of potentially hazardous wastes have been generated that have highly variable characteristics depending on the industry concerned. While some of these wastes contain potentially valuable nutrients, many also contain toxic concentrations of metals, organics and other hazardous compounds (Cameron *et al.*, 1997). Regulations controlling the disposal of hazardous waste are becoming restrictive and the cost of landfilling is becoming prohibitively expensive (Cameron *et al.*, 1997). As a result the concept of land application of industrial wastes and by-products is gaining favour as a cost-effective method of disposing of the waste while dispersing and reducing its potential environmental risk. For the purposes of this discussion, the focus will be on industrial processing wastes and will exclude consideration of organic wastes, such as biosolids.

A number of related terms exist to describe the practice of applying waste to land. The most commonly used is arguably 'land application' (also known as land treatment (Overcash and Pal, 1979)). Miller and Miller (2000) define land application as "the addition of by-products to soil for the purposes of improving crop growth, either through addition of nutrients or improvement of soil physical or chemical properties, either in the short or longer term". Overcash and Pal (1979) define land application as "the intimate mixing or dispersion of wastes into the upper zone of the soil-plant system with the objective of microbial stabilisation, adsorption, immobilisation, selective dispersion or crop recovery, leading to an environmentally acceptable assimilation of the waste". A similar definition to that of Overcash and Pal (1979) was used by Cameron *et al.* (1997).

Another term that refers to the application of waste to soil is 'land disposal'. While no specific definition for this term was found, it implies that waste is applied to a soil for the purposes of disposal rather than as a soil ameliorant. In this sense the definition given by Overcash and Pal (1979) better reflects the intent of this practice than the definition given by Miller and Miller (2000). For purposes of this discussion the terms will be used

interchangeably, but the primary focus is on land disposal, where the objective is to use the soil to dispose of maximum amounts of waste without causing negative impacts to the soil and surrounding environment.

Although landfilling can be considered as a form of land disposal (Overcash and Pal, 1979), Buyeye (2005) argued that landfill constitutes a closed system, whereas land disposal is an open system. Landfills confine wastes to a specified area, usually with a barrier to contain leachates and minimise waste dispersal, whereas land disposal offers the potential to 'treat' waste in the soil, allowing the dispersion and interaction of waste constituents within the soil system.

## 5.2 Considerations for land disposal

Land disposal as a waste treatment technology is not without risk, since applying waste to soil may lead to reduced soil aeration and infiltration (due to clogged pores), salt build-up and even metal toxicity (Buyeye, 2005). Cameron *et al.* (1997) investigated the types, quantities and characteristics of wastes produced in New Zealand and Australia and presented an overview of their potential for land application. They concluded that land disposal was not a suitable option for the reasons highlighted above and that a considerable amount of research was needed if this disposal option was ever to become viable. They do indicate that the use of certain types of wastes (e.g. agricultural wastes, sewage sludge, fly-ash, smelter slag) as soil amendments is feasible if precautions are in place to reduce any potential adverse impacts.

The disposal of industrial wastes should only be conducted in a fashion that does not lead to negative impacts on the soil and any surrounding environments. Overcash and Pal (1979) presented an overview of soil parameters that must be considered when applying wastes to land. These include, *inter alia*, soil type, texture, mineralogy, structure and various physical properties (e.g. bulk density, porosity, hydraulic properties), chemical properties (e.g. pH, cation exchange capacity, base saturation, fertility) and biological properties. Similarly the properties of the waste itself should be considered to determine the potential of the receiving soil to assimilate the waste (Miller and Miller, 2000).

Basta *et al.* (2005) present an overview of some of the key processes involving waste applied to soil. These include sorption of cation and oxyanion species by Fe and Mn oxides, reactions of cations and anions with organic matter and the formation of precipitates of trace elements with anionic compounds. The extent of these reactions and how they are altered in the soil depends on the specific properties of the waste and the soil, with the properties of the soil:waste mixture typically representing some intermediate phase between the soil and waste.

Often, to simulate the effect of the toxic components found in a waste whilst removing other interfering factors, researchers apply salts of the element of concern to soil and measure the availability relative to the concentrations of the salt initially added. Basta *et al.* (2005) indicated that interpretation of these data may be inappropriate due to 'the salt effect'. This occurs when the metal, which is applied to the soil as a soluble salt, shows greater bioavailability compared to the same concentrations of the metal added as a waste. The reasons for this are varied, but typically relate to the form or species of the target element and other properties of the waste that may either reduce or increase mobility of an element in the mixed system. Another consideration highlighted by Basta *et al.* (2005) is 'the plateau effect'. This suggests that if a waste is applied at sufficiently high rates or frequently enough, the properties of the soil may start to resemble that of the waste. Under these conditions it is expected that the maximum availability of a contaminant will be similar to that of the pure waste and increasing application rates are not likely to lead to increases in the bioavailability or sorption of contaminants.

Cameron *et al.* (1997) and Basta *et al.* (2005) suggest four research needs if land application of wastes is to become a feasible disposal technology. These are:

1. More detailed and comprehensive characterisation of wastes and factors affecting release rates of elements from a waste. This will assist in the development of more suitable, environmentally safe and agronomically appropriate land application systems.
2. A better understanding of the physical, chemical and biological processes that determine the fate of a waste in the soil. There are many soil characteristics and processes that can lead to contaminant fixation or dispersal in that system. An in-depth quantitative understanding of these processes will lead to the development

of optimised waste application rates, frequency and timing of application and appropriate selection of locations for waste application.

3. An improved understanding of the impacts of applying a waste to land, on soil, water and air resources. These should ideally be measured rather than inferred from laboratory and field-scale investigations.
4. Improved modeling to better predict the fate of a waste and the processes that are likely to be involved. This requires a multi-disciplinary approach and integrated knowledge of all the processes involved in the soil/plant/animal/atmosphere system.

Unfortunately, the high cost and time required to conduct such extensive, large-scale investigations limit the use of the above approach by industries that typically require cost-effective and immediate solutions to ever-increasing waste disposal problems.

### **5.3 Land disposal: A legal perspective**

In general much of the same legislation discussed in Section 2.4 can be applied here. Sections from the National Water Act (NWA), the NEMA and the ECA all require that pollution should be prevented as far as possible and that those liable for causing pollution will be held responsible for the remediation thereof.

More specifically the NWA gives the Minister authority to prescribe standards and allows the Minister to prescribe outcomes that must be achieved through management practices for the treatment of a waste before it is discharged or deposited into a water body, and that such practices should be monitored (Glazewski, 2005). The NWA defines waste to include "...any solid material or material that is suspended, dissolved or transported in water (including sediment) and which is spilled or deposited on land or into a water resource in such volume, composition or manner as to cause, or to be reasonably likely to cause, the water resource to be polluted...". Though not directly related to land disposal the application of this legislation is likely to impact on the land application of waste, as ultimately there will be concern for contamination of water resources.

In terms of the Environmental Conservation Amendment Act (Act 50 of 2003), waste can only be disposed of at a disposal site that has a permit issued by the Minister of Environmental Affairs and Tourism (Department of Water Affairs and Forestry (DWAF), 2005). The disposal site must be located, designed, operated and monitored in accordance with the conditions issued in the permit. The conditions will include the guidelines set out in the minimum requirements (DWAF, 2005). According to these guidelines, the toxicity of a waste can be assessed using any approved extraction method, but recommends the use of the TCLP procedure (for disposal at general purpose landfill sites) or the acid rain procedure, in the case of mineral waste disposal sites. The primary purpose of the TCLP and acid rain extractions in terms of the requirements of the ‘Waste management series - The minimum requirements for the classification, handling and disposal of hazardous waste’ (‘the minimum requirements’) is to determine the leaching potential of elements from a waste for purposes of disposal to landfill (DWAF, 2005). The TCLP extraction aims to mimic the effects of organic acids present in municipal landfill sites, while the acid rain extraction is for use at dedicated mineral waste disposal facilities. However, these methods, notably the TCLP extraction, are used widely to assess the potential toxicity of a waste and contaminated soils (Al-Abed *et al.*, 2006; Sun *et al.*, 2006). These extractants give an estimate of the ‘estimated environmental concentration’ (EEC), which is considered a ‘worst case scenario’ for a contaminant moving into the environment, typically in water (DWAF, 2005). The EEC values are then compared to the limits stipulated in ‘the minimum requirements’ (DWAF, 2005). These criteria are referred to as the ‘acceptable environmental exposure’ (AEE) and the ‘acceptable human health exposure’ (AHHE; DWAF, 2005; see Section 4.2.2.4).

The guidelines set out in the ‘minimum requirements’ form part of DWAF’s “Waste Management Series” and have the objective of protecting the environment while limiting the impact of poor waste disposal practices. This Series sets out the requirements for the disposal of waste to landfill, where the nature of the waste will be the determining criterion as to the type of landfill. The techniques and principles presented in these guidelines will assist in assessing the hazardous nature of a waste as well as possible treatment technologies to reduce the risks associated with a waste. It does not consider the potential for land disposal of waste as used in the context of this study, and (indeed) stipulates that land treatment may not be used as a treatment technology except in the case of historical or accidental contamination. The reason given for this is that the mechanisms involved in the

attenuation of contaminants from land-applied waste are not well understood and as a precautionary approach the technology is discouraged. This is in line with the comments regarding research needs for land treatment technologies given by Cameron *et al.* (1997) and Basta *et al.* (2005).

## 5.4 Conclusions

Considering that land disposal of waste is not legally permitted in South Africa, one then questions the usefulness of this type of research that investigates the effects of waste on the environment when land applied. However, if the use of land disposal technology is unacceptable due to lack of research and understanding of the impacts and mechanisms involved, then it is a logical argument that this form of research should be used to fill the knowledge gaps, as highlighted by both Cameron *et al.* (1997) and Basta *et al.* (2005). Surely, as the processes involved and the likely impacts become better understood, the feasibility of land disposal increases as waste application rates can be maximised with lower risk to the environment. It is almost inevitable that at some point in the future this technology will be used more widely, as landfill becomes more limited and expensive. It is accepted that not all wastes are equal, with some possessing characteristics that lend themselves to various aspects of land application, while others are of such a hazardous nature that they require very careful management to prevent environmental contamination. While the risks associated with some wastes are very clear (e.g. radioactive waste) there are those where this distinction is not as well defined. The level at which these wastes cause a problem in a soil (and surrounding environment) can only be assessed by laboratory and field-based research. In this research two Mn-rich processing wastes are investigated for their potential for land disposal. As outlined in Chapter 1, the ameliorative approaches originally proposed for the remediation of these two wastes were not considered feasible. The disposal of the wastes to land was viewed as a viable method to dispose of these wastes, thereby reducing the long-term cost associated with maintaining and monitoring of the dedicated disposal sites used at present.



## **CHAPTER 6**

### **THE CHARACTERISATION OF TWO MANGANESE-RICH PROCESSING WASTES**

#### **6.1 Introduction**

The two Mn-ore processing wastes discussed in Chapter 1, namely the Mn-rich siliceous-slag (SS) and the Mn-rich electro-winning waste (EW), were investigated in this part of the study. The SS is a by-product from the smelting of Mn-rich ores along with fluxes (typically lime and silica) added during the smelting process. The EW is the by-product after Mn-rich ores are solubilised in sulphuric acid. Various conditioners are added during the electrolytic recovery process (including ammonia and lime), resulting in a waste that contains high amounts of residual Mn, N, Ca and S. After electrolytic recovery of the Mn, the residue is passed through a belt-filter press to remove excess liquid and the solid waste is disposed of at a dedicated disposal site.

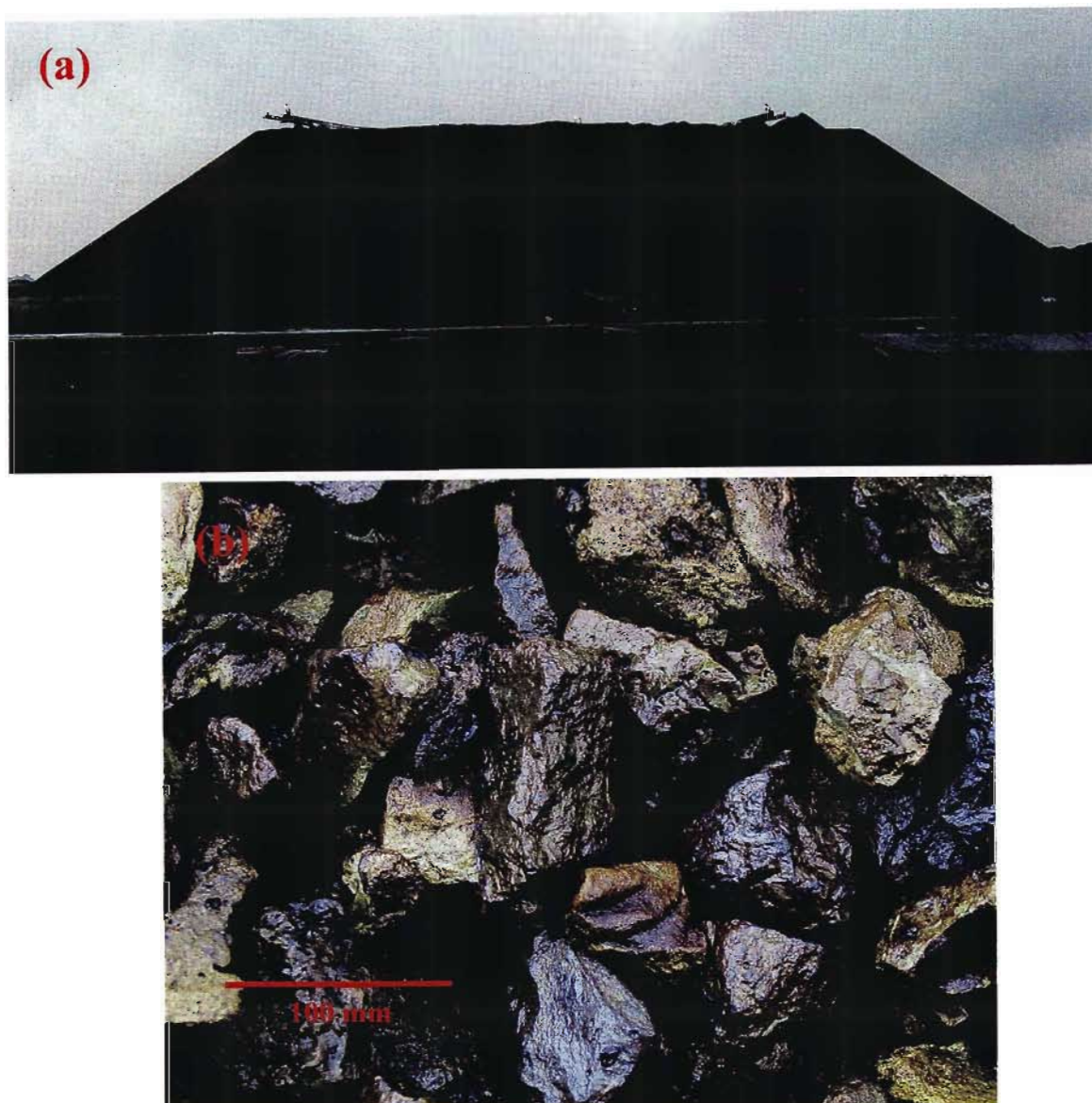
To assess the potential of a waste for land disposal, as well as to gain insight into the likely negative impacts that a waste may have on soil properties, a detailed analysis of the waste is required. This typically entails batch extractions under laboratory conditions. To this end a detailed chemical analysis of the SS and EW was conducted and consideration was given to likely impacts of applying these wastes to soils, as well as a consideration of some of the mechanisms that are likely to be involved in the reactions of the waste in the soil environment.

#### **6.2 Materials and methods**

##### 6.2.1 Waste material collection and preparation

The SS was collected as coarse aggregates (from about 50 to 100 mm) directly from the conveyor belts that moved slag onto the dedicated slag disposal heap on the Samancor property (Meyerton, Gauteng, South Africa; Plate 6.1). Material was shoveled into nylon bags and transported to the University for further handling. The SS was air-dried before being crushed with a metal stamper to pass through a 2 mm sieve and stored in a black plastic bin for further use.

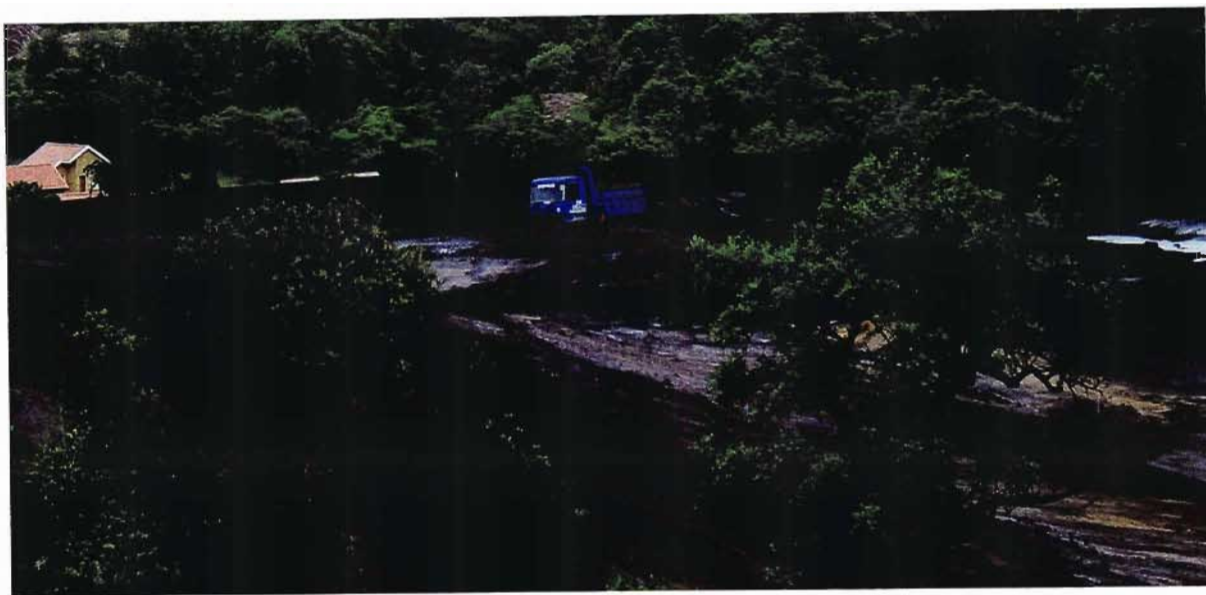
Electro-winning waste (Nelspruit, Mpumalanga, South Africa; Plate 6.2) was collected, by MMC staff, from the processing plant waste stream into a large woven nylon bag and delivered to the University. The material was air-dried and milled to pass through a 2 mm sieve and stored in large black plastic bins for further use.



**Plate 6.1** The (a) slag-heap at Samancor and (b) a close-up of the slag.

#### 6.2.2 Physical and chemical characterisation of the wastes

The determinations of the basic chemical properties of the SS and EW followed those described in Section 4.2.1.2. In addition, exchangeable acidity and Al were measured according to Sims (1996), with Al being measured by AAS. Particle size and particle density were determined by the methods described in Section 4.2.1.3.



**Plate 6.2** The MMC electro-winning waste disposal site (Pappas Quarry, Nelspruit, Mpumalanga, South Africa), showing a view overlooking the quarry.

### 6.2.3 Mineralogy

The mineralogy of the SS and EW was determined as described in Section 4.2.1.4. Light microscope images (Leica MZ16 with JVC digital Camera and Auto-Montage image capture software) of the SS were also captured.

### 6.2.4 Fractionation investigation

Sequential extraction procedures (fractionation procedures) attempt to partition elements into operationally defined geochemical fractions (Gleyzes *et al.*, 2002). These include soluble and readily exchangeable, weak acid soluble, reducible, oxidisable, and residual fractions. Despite the many criticisms of these methods they remain a valuable tool to determine approximate partitioning of phases in a material, thereby improving the prediction of element availability and mobility (Gleyzes *et al.*, 2002). A five-step batch-wise fractionation procedure (Johnston and Petras, 1998) was used to determine soluble and exchangeable (EX; 0.05 M  $\text{CaCl}_2$ ), inorganically bound (IB; 2.5% (v/v) acetic acid ( $\text{CH}_3\text{OOH}$ )), organically bound (OB; 0.1 M potassium pyrophosphate ( $\text{K}_4\text{P}_2\text{O}_7$ )), and bound to amorphous oxides (AMOX; acid oxalate (1:3 ratio of 0.2 M  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and 0.23 M  $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  adjusted to pH 3)) amounts of Co, Cu, Fe, Mn, Ni, Pb and Zn.

Elemental solution concentrations were determined by AAS. The final step (residual, HCl-HF digestion) was omitted.

To assess the difference between water-soluble Mn and CaCl<sub>2</sub>-extractable Mn, additional samples of EW were extracted with either distilled water or 0.05 M CaCl<sub>2</sub>, at different waste:solution ratios.

#### 6.2.5 Effect of pH on dissolution of the wastes

The SS and EW were extracted with solutions of varying pH. Solutions with pH 0.5, 1, 3, 5, 7, 9 and 11 were obtained by adjusting the pH of distilled water using HCl or NaOH. Thirty mL of each solution was added to a 6 g sample (< 0.5 mm) of either SS or EW, the mixture shaken on an end-over-end shaker (30 r.p.m.), at 24 °C for 16 hrs, centrifuged at 3000 r.p.m. and filtered. No attempt was made to control solution pH or CO<sub>2</sub> pressure during the extraction. The pH of the extract was measured and concentrations of Ca, S, Mn, Fe and Mg determined by ICP-OES. The Pb concentration of the EW extracts was also determined by ICP-OES, but omitted for the SS due to low total concentrations (Section 6.3.2). The Si concentration of the SS extracts was determined by the method of Fox *et al.* (1969).

#### 6.2.6 Phosphorus sorption

The P sorption capacity of the SS and the EW was determined by the method described in Section 4.2.1.5.

### **6.3 Results and discussion**

#### 6.3.1 Basic chemical and physical properties

The SS was very alkaline, while the pH of the EW was near-neutral (Table 6.1). The low EC of the SS indicated low amounts of soluble salts, whereas the EW had a remarkably high EC, indicating potential problems with respect to salinity (see Section 6.3.3). The OC content of both wastes was low. The concentrations of ammonium and nitrate could not be determined in the EW using the TRAACS 2000 auto-analyser due to Mn-precipitates

forming in the tubes of instrument. In the SS both available and total N concentrations were low. Total N in the EW was very high, attributed to the presence of ammonium sulphate salts. The distillation procedure was used to determine the amount of N, bound as ammonium, in the EW. It was found that there was  $8813 \text{ mg kg}^{-1}$  N as ammonium, i.e., 95% of the N in the EW was in this form.

The SS generally had low amounts of extractable base cations, with only Ca being present in any appreciable amount. The EW had a high concentration of extractable Ca and low concentrations of extractable Mg, Na and K. The CEC of both materials was low, though the CEC of the EW was about 3-fold higher than that of the SS. The discrepancy between the CEC and sum of base cations in the wastes shows that there was solubilisation of base cation-rich compounds. As expected the SS had no detectable exchangeable acidity and it was slightly elevated in the EW. The SS had a very low concentration of exchangeable Al, while it was considerably higher in the EW. This indicates some acid-producing potential of the EW. The SS has reasonable potential as a liming agent, reflected in the moderate CCE and high pH.

Both the SS and EW had high particle densities; the particle density of the EW being higher than that of the SS (Table 6.2). The particle size distribution of the SS only reflects the characteristics of the material used in this investigation, as the material was crushed from large solid aggregates. The extent of the crushing procedure would determine the amount of fines within the crushed product, and is likely to vary for every new batch of material crushed. In this instance the SS was found to be predominantly coarse sand with high amounts of medium and fine sand (Table 6.2). The EW was loosely aggregated and required little effort to mill and more realistically reflects the textural characteristics of the waste. The EW was fine in texture, consisting predominantly of silt, with high amounts of fine sand and a moderate amount of clay-sized particles (Table 6.2).

### 6.3.2 Total elements

The SS consisted primarily of Mn, Ca and Si, and had notable concentrations of Mg, S, Ba and Sr (Appendix 6.1). Concentrations of other trace elements tended to be low, with many being below detection limits. The EW had high total concentrations of Fe, Mn and S, with appreciable concentrations of As, Ba, Ca, Cu, Ni, Pb, Sr, V and Zn (Appendix 6.1).

**Table 6.1** Basic chemical characteristics of slag (SS) from the Samancor Mn-smelter and electro-winning waste (EW) from MMC

Parameter		SS	EW
pH	H <sub>2</sub> O	9.73	6.89
	1 M KCl	9.81	6.86
Electrical conductivity (25 °C)	(mS m <sup>-1</sup> )	35.8	1735
Organic carbon	(g 100g <sup>-1</sup> )	0.72	0.56
AMBIC P	(mg kg <sup>-1</sup> )	5.26	1.22
NH <sub>4</sub> <sup>+</sup> -N	(mg kg <sup>-1</sup> )	6.32	nd
NO <sub>3</sub> <sup>-</sup> -N	(mg kg <sup>-1</sup> )	2.90	nd
Total N	(mg kg <sup>-1</sup> )	391	9246
Extractable base cations (cmol <sub>c</sub> kg <sup>-1</sup> )	Ca	13.2	71.0
	Mg	3.97	1.76
	Na	0.23	1.31
	K	0.22	0.06
Cation exchange capacity	(cmol <sub>c</sub> kg <sup>-1</sup> )	3.42	9.50
Exchangeable acidity	(cmol <sub>c</sub> kg <sup>-1</sup> )	bd	4.47
Exchangeable Al	(cmol <sub>c</sub> kg <sup>-1</sup> )	0.24	1.28
Calcium carbonate equivalence	(%)	40.2	12.6

nd not determined.

bd below detection.

**Table 6.2** Basic physical properties of slag (SS) from the Samancor Mn-smelter and electro-winning waste (EW) from MMC

Parameter	SS	EW
Particle density (g cm <sup>-3</sup> )	3.30	4.40
<b>Particle size (%)</b>		
Coarse sand (0.5 – 2 mm)	48.2	0.70
Medium sand (0.25 – 0.5 mm)	16.6	1.10
Fine sand (0.053 – 0.25 mm)	26.7	27.6
Silt (0.002 – 0.053 mm)	7.10	58.6
Clay (< 0.002 mm)	1.40	12.0

Typically it is expected that the sum of the major element composition would be about 100%, but for both the SS and EW, the total values were lower (Appendix 6.1). This was attributed to the elevated S concentration of the wastes (about 1.5 and 20.8% for the SS and EW, respectively), which is not considered in determining the sum value. Including these amounts of S into this value present a more realistic value for total elements (97.8 and 100.1% for the SS and EW, respectively).



6.3.3 Saturated paste extracts

The SS had low concentrations of soluble metals (Table 6.3). The only elements in appreciable concentrations were S and Ca. Moderate amounts of Na were also measured. The EC of the SS was elevated, though the SAR was low (Table 6.3). The EW had high concentrations of soluble elements, notably Mn, S, Ca, Mg and Na, and elevated concentrations of soluble Co, Ni and Sr, this reflected in the very high EC value. Hillel (1998) indicates that a soil is usually considered saline if the EC of the saturated paste extract exceeds 400 mS m<sup>-1</sup>. In this instance the EC of the paste extract (and also the EC of the 1:2.5 EW:water extract) were markedly higher, indicating potential salinity problems. Keren (2000) reports salinity classification criteria for irrigation water, where 0 to 400 mS m<sup>-1</sup> is classed as low salinity, 400 to 1200 as moderate salinity, 1200 to 2250 as high salinity and 2250 to 5000 as very high salinity. In this instance the EC value results in a very high salinity classification.

**Table 6.3** Analysis of saturated paste extracts of slag (SS) from the Samancor Mn-smelter and electro-winning waste (EW) from MMC

Sample	Al	Ba	Cd	Co	Cr	Cu	Fe
	(mg L <sup>-1</sup> )						
SS	3.33	0.14	bd	bd	0.01	0.12	bd
EW	0.03	0.05	0.01	71.70	bd	0.28	0.06
	Mn	Ni	P	Pb	S	Sr	Zn
SS	0.61	bd	0.25	bd	502	2.43	bd
EW	9835	10.8	0.07	0.73	31815	13.4	1.13
	Ca	Mg	Na	K	EC	SAR	SP
	(cmol <sub>c</sub> L <sup>-1</sup> )				(mS m <sup>-1</sup> )		(%)
SS	2.56	0.03	1.12	0.13	244	0.99	17.7
EW	3.74	23.5	4.06	0.25	6780	1.10	50.0

bd below detection.  
EC Electrical conductivity.  
SAR Sodium adsorption ratio.  
SP Saturation percentage.

While total and extractable Ca concentrations were considerably higher than those of Mg (Appendix 6.1 and Table 6.1, respectively), there was a markedly higher concentration of soluble Mg in the EW. This was attributed to the presence of soluble ammonium and/or

magnesium-sulphate salts in the EW, while the Ca existed as the less soluble mineral gypsum (Section 6.3.6). The high concentrations of soluble salts in the EW are reflected in the exceptionally high EC of the waste. The SAR was low, a result of the high Ca and Mg concentrations. The high concentrations of soluble salts suggest high potential for salinity-induced problems and possibly metal leaching (Mn and Co) if the material is applied to land.

6.3.4 Extractable elements

Plant available (DTPA-extractable) concentrations of metals in the SS were low except for Mn, which was about 3.5-fold higher than that reported for South African soils (Table 6.4). The EW also had a very high concentration of extractable Mn and an elevated concentration of Co, which were also considerably higher than the typical concentrations of these metals in South African soils (Table 6.4). Concentrations of Cu, Ni and Zn in the EW were also slightly elevated but not at levels that would suggest likely toxicity problems.

**Table 6.4** Diethylenetriaminepentaacetic acid-extractable metal concentrations in the slag (SS) from the Samancor Mn-smelter and electro-winning waste (EW) from MMC and ethylenediaminetetraacetic acid (EDTA)-extractable metal concentrations of surface soils in South Africa

Sample		Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
		----- (mg kg <sup>-1</sup> ) -----								
	SS	bd	1.11	bd	0.14	3.29	832	0.02	0.09	3.12
	EW	bd	69.5	bd	17.9	1.02	5708	5.57	1.38	7.39
South African surface soils <sup>†</sup>	Mean (n > 4300)	0.02	3.63	0.16	2.87	448 <sup>‡</sup>	234 <sup>‡</sup>	2.39	3.32	1.66
	Minimum	bd	bd	bd	bd	na	na	bd	0.02	bd
	Maximum	1.46	48.9	12.5	67.3	na	na	170	109	210

<sup>†</sup> Herselman *et al.* (2005).  
<sup>‡</sup> Median (n = 514) values for rangeland topsoils in the Mpumalanga Highveld in South Africa (Steyn and Herselman, 2006).  
bd below detection.  
nd not determined.  
na Data not available.

As discussed previously the TCLP and acid rain extractions are the preferred extractants for classification purposes for disposal of hazardous waste to landfill (Sections 5.3). The



primary element of concern here is Mn as the concentration measured in the TCLP extract of the SS (302 mg L<sup>-1</sup>) far exceeds both the AEE and AHHE limits (Table 6.5). The acid rain procedure extracted considerably less Mn than the TCLP method. This may be related to the high pH buffering capacity of the acetic acid (resulting in a lower equilibrium pH than the acid rain extract) as well as the metal complexing ability of the acetic acid solution. Concentrations of other metals were low, and probably of little concern, except for the elevated amounts of TCLP-extractable Pb in the SS, that exceeded the AEE and AHHE limits by about two-fold.

**Table 6.5** Final solution pH and concentrations of metals in the slag (SS) from the Samancor Mn-smelter and electro-winning waste (EW) from MMC, extracted with TCLP and acid rain solutions. The AEE<sup>†</sup> and AHHE<sup>‡</sup> are included for comparative purposes

Sample	Extract	Final pH	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
			-----( $\text{mg L}^{-1}$ )-----								
SS	TCLP	7.81	bd	bd	bd	bd	bd	302	0.04	0.25	bd
	Acid rain	8.29	0.02	0.01	bd	0.06	0.02	2.58	0.06	0.01	bd
EW	TCLP	5.09	bd	4.21	bd	0.75	0.07	686	0.88	0.53	3.87
	Acid rain	7.32	0.05	1.81	bd	0.02	0.10	217	0.45	0.39	0.37
	AEE		0.03	0.97	4.70	0.13	9.00	0.30	0.75 <sup>¶</sup>	0.12	0.83
	AHHE		0.04	0.70	-	2.30	-	4.90	0.18 <sup>¶</sup>	0.02	11.0

† Acceptable environmental exposure (DWAF, 2005).  
‡ Acceptable human health exposure (DWAF, 2005).  
¶ Soluble nickel salts (DWAF, 2005).  
bd below detection.

It is likely that in the case of the TCLP-extraction that organo-metal complexes were formed resulting in the higher concentrations of Pb measured than for the acid rain extraction. However, under conditions of land-application it is unlikely that this amount of Pb would be problematic, especially in the light of the low total amount (Appendix 6.1) and that the SS would be diluted with soil, further reducing the amount of available Pb.

The concentration of Mn extracted from the EW, by both the TCLP and acid rain solutions, were very high, these values exceeding the limits imposed by the ‘minimum requirements’ (Table 6.5). As with the SS, the TCLP extraction removed higher amounts of Mn than the acid rain extraction. A number of other metals were also measured at concentrations over

the AEE and AHHE limits (notably Co, Ni and Pb). Again the TCLP solution resulted in a lower equilibrium pH when compared to the acid rain extraction.

### 6.3.5 Fractionation

In the sequential extraction the SS had lower concentrations of EX metals than the EW (Table 6.6).

**Table 6.6** Analysis of the batch-wise fractionation of the slag (SS) from the Samancor Mn-smelter and electro-winning waste (EW) from MMC. Element concentrations are given in mg kg<sup>-1</sup>

Sample	Mn	Fe	Zn	Co	Cu	Pb	Ni
<b>Exchangeable (0.05 M CaCl<sub>2</sub>) - EX</b>							
SS	32.4	2.72	1.46	bd	4.09	9.50	bd
EW	10437	3.54	1.67	59.1	4.91	10.9	16.8
<b>Dilute acid extractable (2.5 % (v/v) acetic acid) - IB</b>							
SS	41271	15.1	6.38	bd	bd	14.4	bd
EW	24106	814	208	199	139	13.9	34.4
<b>Organically bound (0.1 M K<sub>4</sub>P<sub>2</sub>O<sub>7</sub>) - OB</b>							
SS	3711	54.7	19.5	10.1	5.07	39.1	11.4
EW	16380	1507	56.9	116.2	136	119	bd
<b>Amorphous oxide bound (acid oxalate adjusted to pH 3) - AMOX</b>							
SS	15835	3067	49.4	53.4	bd	bd	bd
EW	14448	65373	324	271	257	172	bd

bd below detection.

In the case of the EW, the EX amount of Mn was very high, while concentrations of Co, Pb and Ni indicated some readily available forms of these metals. Manganese, Co, Ni and, to a lesser extent, Pb concentrations in the saturated paste extracts indicated that these elements were in water-soluble forms in the EW. The comparison of water-soluble and CaCl<sub>2</sub>-extractable Mn in the EW showed that the extractable Mn exists in a readily soluble form, with little difference between the Mn concentrations extracted at the different waste:solution ratios, except perhaps at the lowest waste:solution ratio (1:10), where the 0.05 M CaCl<sub>2</sub> extracted slightly more Mn than the water did (Appendix 6.2).

The concentrations of IB-Mn (and to a far lesser extent, Fe, Zn and Pb) in the SS were higher than the EX fraction. It was noted that after extraction with the low pH solution (acetic acid), a silica-gel formed (confirmed by EDX analysis), confirming the dissolution of the predominant mineral that contained high amounts of Mn (Section 6.3.6). The concentrations of all IB-metals in the EW were higher than in the EX fraction. Considering that the extraction procedure was conducted in a batch-wise fashion, the dilute acid extractable metal concentrations may also reflect soluble and exchangeable fractions (the same notion applying to all other extractants used). These results suggest that, in addition to the high soluble fraction of Mn in the EW, there was a high amount of acid soluble Mn. If the EX Mn fraction is deducted from the IB Mn fraction, then about 13 600 mg kg<sup>-1</sup> is estimated to be dilute acetic acid-soluble. It is likely that these metals were released, due to dissolution reactions, from the lattice structure of the primary mineral oxides, jacobsonite and magnetite (Section 6.3.6).

In the SS, the concentration of OB-Mn was lower than the IB-Mn, while all other OB-metal concentrations were higher than in the IB-extractable fraction. The concentration of OB-Mn in the EW was high, as were the concentrations of Fe, Co, Cu and Pb. Nickel concentrations were below detection in the OB fraction of the EW. The high concentrations of some metals in the OB fraction were unexpected considering the low amount of organic matter in the wastes. In the soil environment, pyrophosphate ions promote the dispersion of organic colloids in a basic medium, thereby solubilising metal ions (Gleyzes *et al.*, 2002). This suggests that some other mechanism was involved in solubilising metals from the wastes. Gleyzes *et al.* (2002) indicated that at pH 10 there exists the risk of extracting amorphous oxides. The pH of the final extracting solution after treatment, of the SS, with K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> was 11.03 and was 9.58 for the EW, suggesting that extraction of amorphous oxides was possible.

Concentrations of AMOX metals were also high, notably Mn and Fe concentrations. For both SS and EW, the Ni concentrations were below detection, and Cu and Pb were below detection for the SS, possibly due to the formation of sparingly soluble salts with oxalate.

It should be noted that the EW contained about 23% total Mn (calculated from XRF data) and that only a small fraction of this was readily soluble. Water soluble and 0.05 M CaCl<sub>2</sub>-extractable Mn concentrations (Appendix 6.2) ranged from 9 000 to 10 500 mg kg<sup>-1</sup>,

indicating that only about 3.9 to 4.5% of the total Mn was readily available. Similarly only about 10.3% of the Mn was acetic acid-extractable. While these ratios suggest that a relatively small fraction of the Mn is in moderately available form when compared to the total, these concentrations are very high and may pose serious environmental risk. Ross (1994) reports that the total Mn concentration in soil to be considered toxic ranges from 1500 to 3000 mg kg<sup>-1</sup>. The soluble and EX-Mn concentrations of the EW are about three to five-fold higher than this value and about 40-fold higher than the typical value for a rangeland soil in South Africa (Table 6.4). In addition, the data also suggest that, under certain conditions, such as high acidity, the potential exists for the release of very high amounts of Mn from the waste.

### 6.3.6 Mineralogy

The predominant mineralogical component of the crystalline SS was the olivine, glaucocroite (CaMnSiO<sub>4</sub>). Also present were small amounts of quartz. Though not definitive there also appeared to be small amounts of CaO and possibly bustamite ((CaMn)<sub>3</sub>Si<sub>3</sub>O<sub>9</sub>) in the SS. The EW consisted predominantly of jacobsonite (MnFe<sub>2</sub>O<sub>4</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O). There also appeared to be some evidence of barite (BaSO<sub>4</sub>), though weak and overlapping peaks made this assessment difficult. However, analysis of the EW by XRF (Appendix 6.1) and EDX (see below) supported the finding of barite. It was also evident from the XRD pattern of the bulk sample that minor amounts of other minerals were present, but at considerably lower concentrations than the predominant minerals and so these could not be identified in the bulk sample. It was also clear from previous analyses (Section 6.3.3) that the EW had a soluble component. To determine the mineralogical make-up of this soluble fraction the EW was leached (with distilled water) and the resultant supernatant evaporated to dryness at room temperature. This precipitate was then analysed by XRD and found to consist predominantly of ammonium sulphate salts, the likely minerals being mohrite ((NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O) and boussingaultite ((NH<sub>4</sub>)<sub>2</sub>Mg(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O). Other minerals that may have been present in the EW were despujolsite (Ca<sub>3</sub>Mn<sup>4+</sup>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>·3H<sub>2</sub>O) and ilesite ((Mn,Zn,Fe<sup>2+</sup>)SO<sub>4</sub>·4H<sub>2</sub>O), though evidence for the presence of these minerals was not conclusive.

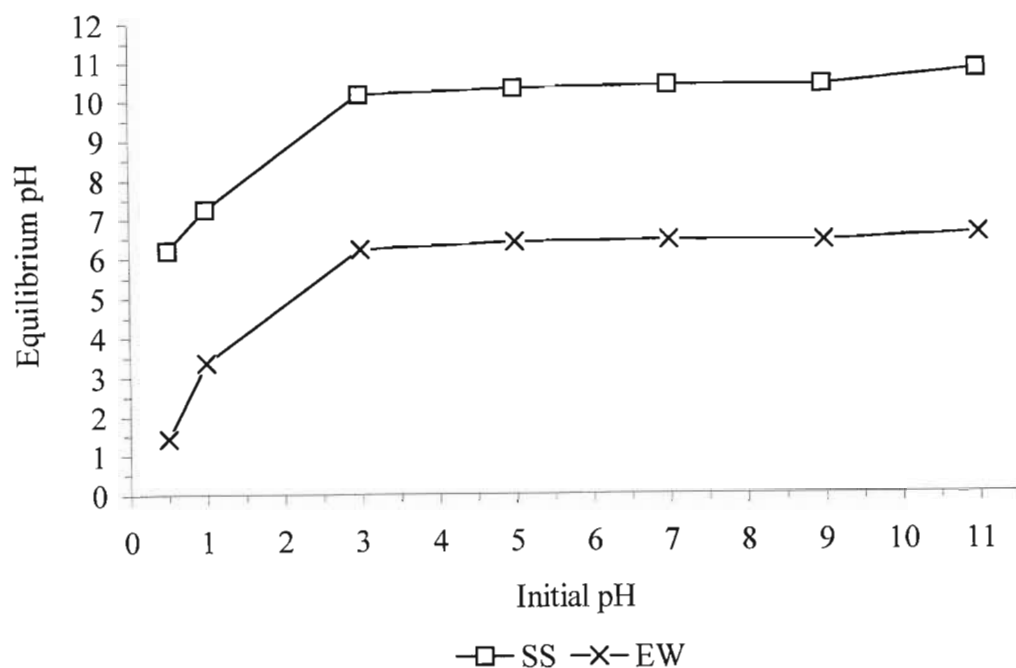
The ESEM images and EDX traces of the SS and the EW are presented in Appendices 6.3 and 6.4, respectively. The fractured surface of the SS was a result of the crushing process,

increasing the surface area of the particles, as well as creating many broken edges, that could enhance mineral dissolution. Light microscope images revealed the general ‘glassy’ appearance of the crushed aggregates (Appendix 6.5), some with smooth surfaces and others showing pitting (possibly due to the formation of gaseous bubbles during the cooling of the molten slag). Qualitative analysis of the SS by EDX revealed that Ca, Mn and Si were the predominant elements (Appendix 6.3), which concurs with the findings of the XRF analysis. In some localised areas, elevated amounts of Ba, Sr and S were found, along with the other more common elements (Ca, Mn and Si). It was, however, not clear if these existed as separate mineral phases (possibly barite) or were contaminants of the major minerals present. The EW was finely divided, appearing to consist of loose aggregations of the various mineralogical fractions, the EDX analysis (Appendix 6.4) supporting the results of XRF and XRD.

It is often difficult to conclusively distinguish between the types of minerals in industrial processing wastes, especially where the chemical make-up is complex. If some phases occur at very low concentrations then identification is difficult. Furthermore, complex substitution of various elements within mineral phases may sufficiently alter XRD patterns to make identification of pure minerals difficult. For instance, Gee *et al.* (1997) reported that many of the mineral phases they found in historical smelting slags were of non-stoichiometric ratios and so they could not identify all phases as known minerals.

#### 6.3.7 Dissolution investigation

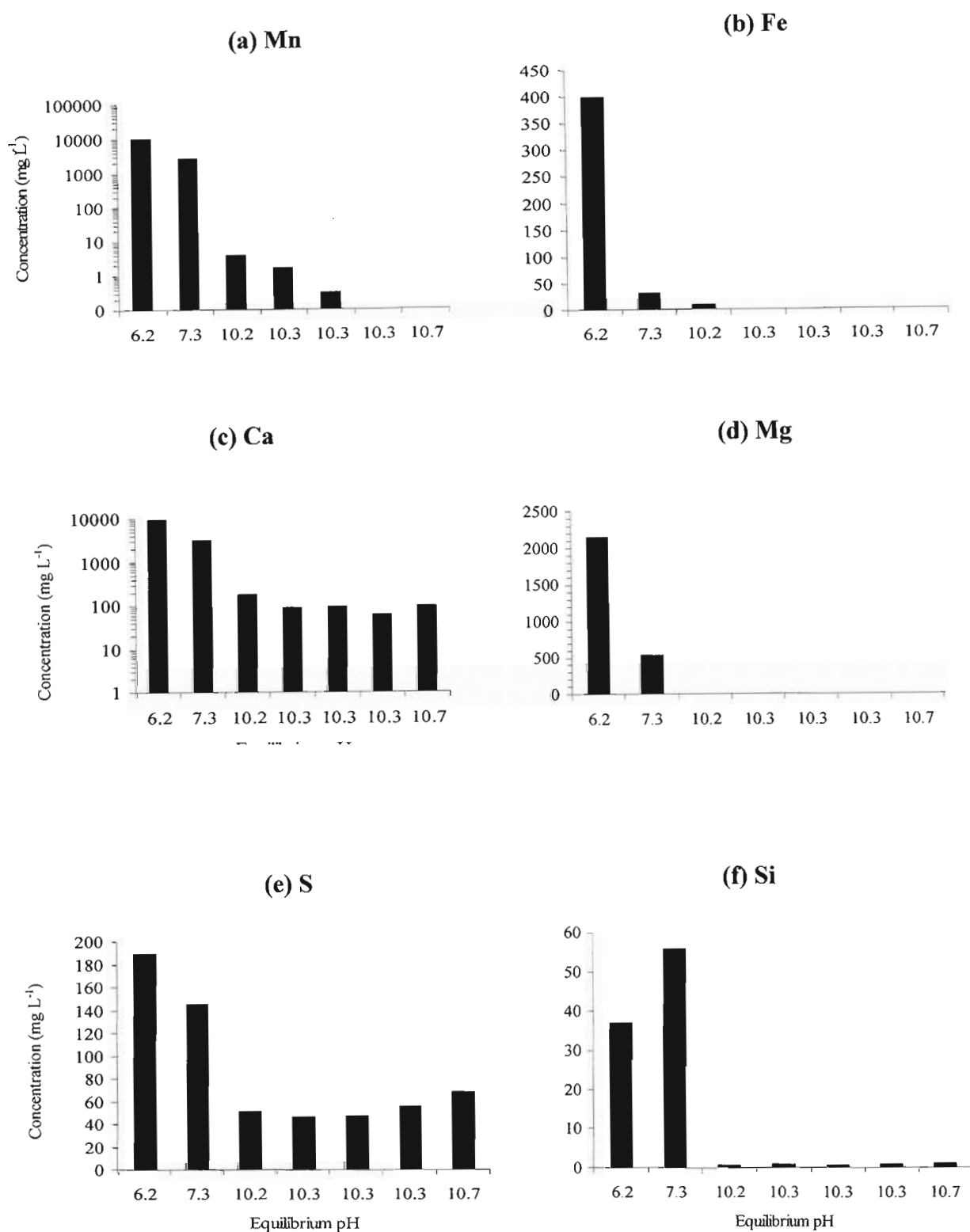
Both waste materials showed a high degree of pH buffering (Figure 6.1). The SS increased the initial extracting solution pH of 0.50 to 6.22 and the initial pH of 1.00 to 7.27 (Figure 6.1). The initial solutions with pH values from 3.00 to 11.0 increased to between 10.2 and 10.7, suggesting that (under these experimental conditions) equilibrium had been attained. The EW buffered at a lower pH than the SS (Figure 6.1). At initial pH values of 0.50 and 1.00 the equilibrium pH values were 1.44 and 3.37, respectively. Thereafter, for initial pH values from 3.00 to 11.0, the equilibrium pH values were between 6.22 and 6.54, again suggesting equilibrium for the given experimental conditions.



**Figure 6.1** Equilibrium solution pH of the slag (SS) from the Samancor Mn-smelter and electro-winning waste (EW) from MMC treated with solutions of different initial pH.

The SS had a high acid-neutralising capacity (ANC), even at low initial pH. This may be accounted for by two possible mechanisms. The waste contains CaO that will hydrolyse to produce hydroxyl ions. While the presence of CaO in the SS was not conclusively confirmed (Section 6.3.6), many authors report variable amounts of CaO in different furnace slags (e.g. Pera *et al.*, 1999; Idris and Saed, 2002; Seggiani and Vitolo, 2003; Shen *et al.*, 2004; Frias *et al.*, 2006). Another mechanism is the dissolution of silicates at low pH, where protons are consumed when displacing the cations (e.g. Mg, Ca, Mn and Fe) that hold silica tetrahedra together (Jonckbloedt, 1998; Gerard *et al.*, 2003).

There were sharp decreases in the concentrations of most elements as pH increased to the apparent equilibrium pH condition ( $\text{pH} > 10.2$ ) in the SS (Figure 6.2). The concentrations of Mn and Ca were similar at pH 6.22 and 7.27, but Mn (Figure 6.2a) decreased to negligible amounts at higher pH, while Ca concentrations (Figure 6.2c) equilibrated between 61.7 and 96.2  $\text{mg L}^{-1}$ . Magnesium (Figure 6.2d) and Fe (Figure 6.2b) behaved in a similar manner to Mn, though concentrations at the lower pH were not as high as Mn or Ca concentrations.



**Figure 6.2** Solution concentrations of (a) Mn, (b) Fe (c) Ca, (d) Mg, (e) S and (f) Si released from the slag from the Samancor Mn-smelter when treated with solutions of varying pH.

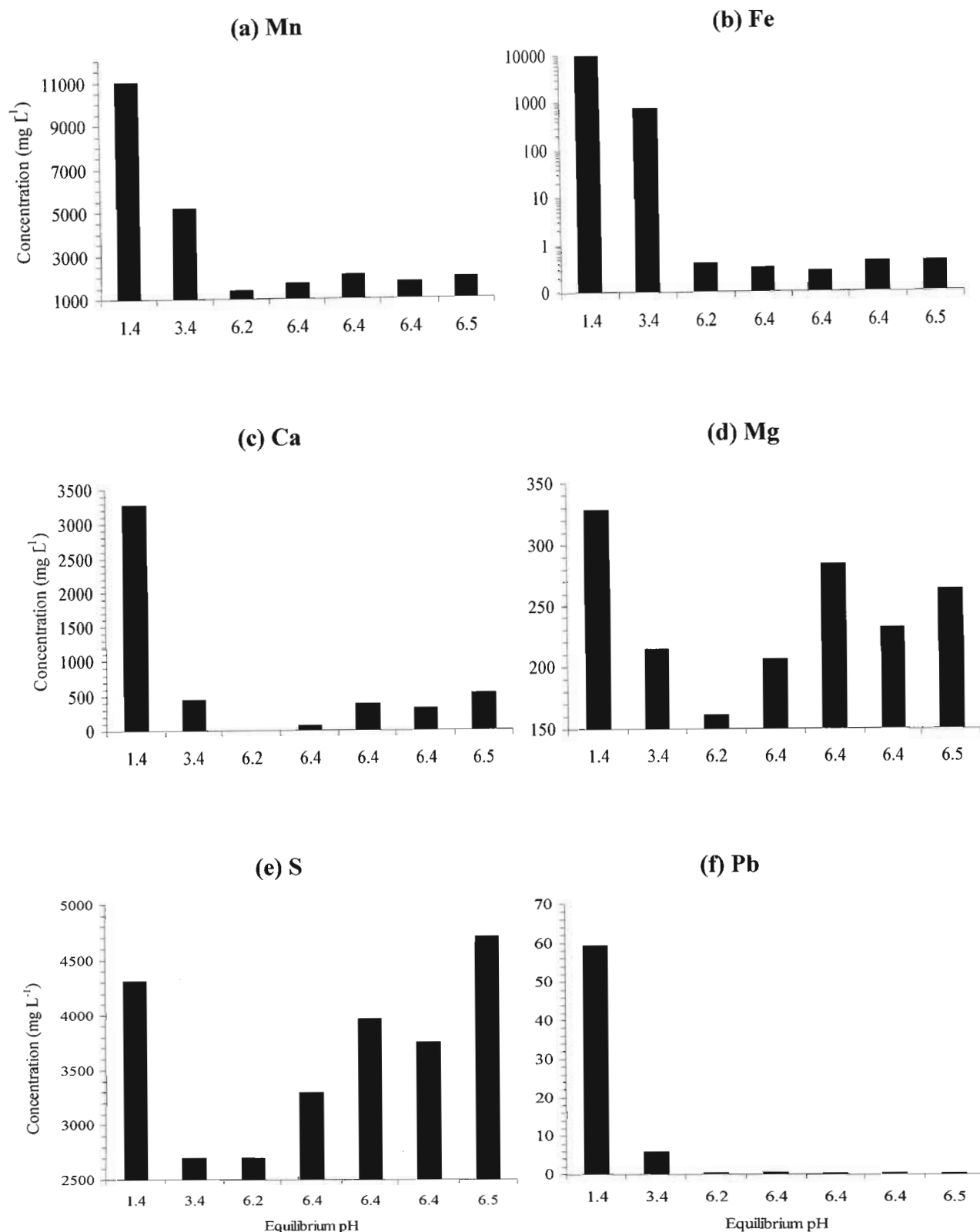
Kato and Owa (1996) examined the dissolution of different slags at varying pH. They report that, at low pH, concentrations of Ca, Mg and Si increased, reflecting the findings for Ca and Mg reported here. Sulphur concentrations of the SS also decreased as pH increased, with equilibrium concentrations of between 46.7 and 67.5 mg L<sup>-1</sup> achieved at the higher pH values (Figure 6.2e). Silicon concentrations increased initially from 36.9 mg L<sup>-1</sup> (at pH 6.22) to 55.5 mg L<sup>-1</sup> at pH 7.27, and then declined to concentrations of < 1 mg L<sup>-1</sup> at pH > 10.2 (Figure 6.2f). The low concentrations of Si measured in the low pH solutions were attributed to the formation of a 'silica-gel' in the extraction vessels (personal observation). Analysis of the gel by EDX confirmed that it was primarily Si, while XRD analysis showed it to have no long-range crystalline order. Jonckbloedt (1998) indicates that Si monomers begin to polymerise as solution concentrations of Si exceed about 100 mg L<sup>-1</sup>, and this could be the reason for the formation of the observed 'silica-gel'.

The ready dissolution of the SS is not surprising considering the generally low stability of olivines in natural environments. The high ratio of divalent cations to Si allows for chemical attack of crystal surfaces, resulting in increased rates of dissolution of silica tetrahedra, thus exposing more surfaces for chemical attack (Huang, 1989). The rate of dissolution under acidic conditions is largely dependant on surface area and H<sup>+</sup> concentration (Luce *et al.*, 1972). Kato and Owa (1996) suggest that, in the slags they studied, the first dissolution step was an ion exchange reaction with H<sup>+</sup> and base cations, followed by the hydrolysis of Si-O-Si and Al-O-Si.

In the EW, concentrations of Mn (Figure 6.3a) and Fe (Figure 6.3b) were highest at the lowest equilibrium pH, the concentrations of both metals decreasing sharply as pH increased, though more markedly for Fe. The concentrations of Fe were all below 0.5 mg L<sup>-1</sup> at pH > 6.22. Manganese reached equilibrium concentrations of between 1 360 and 2 066 mg L<sup>-1</sup> at pH values > 6.22, reflecting the soluble Mn component of the EW (Section 6.3.3). The higher Fe concentrations at low pH were probably due to dissolution of the Fe containing minerals in the EW (magnetite and jacobsite).

Calcium concentrations were highest (3270 mg L<sup>-1</sup>) at the lowest pH but decreased sharply from pH 1.44 to 3.37, the concentrations remaining relatively constant thereafter (Figure 6.3c). This was probably due to dissolution of Ca-containing compounds at the low pH.





**Figure 6.3** Solution concentrations of (a) Mn, (b) Fe (c) Ca, (d) Mg, (e) S and (f) Pb released from the electro-winning waste from MMC when treated with solutions of different pH.

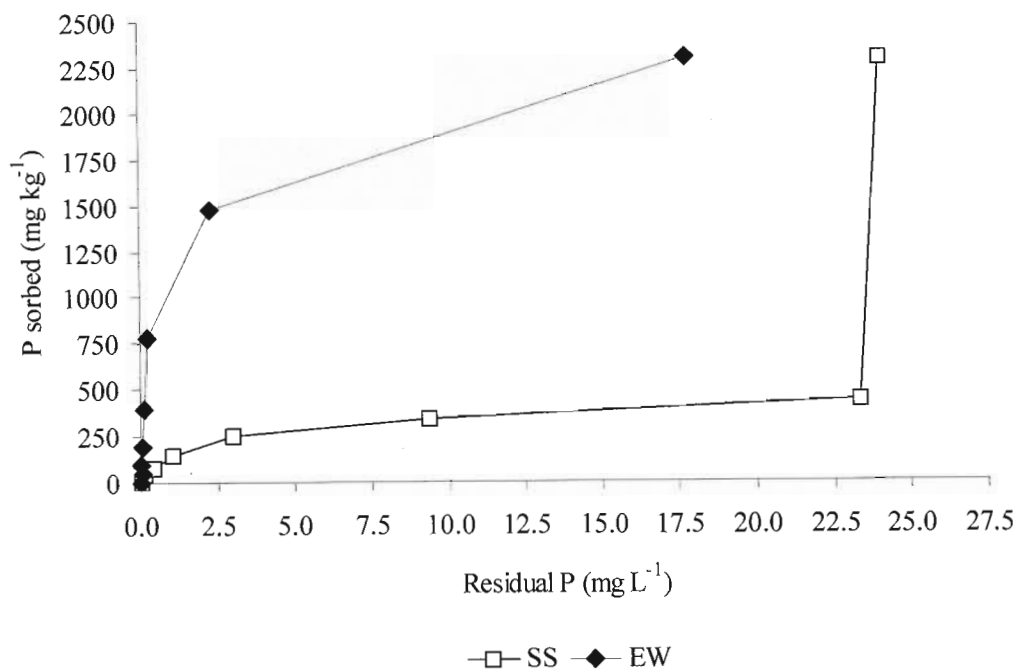
Sulphur concentrations decreased from 4 308 to 2 698 mg L<sup>-1</sup> as pH increased from 1.44 to 3.37, but increased to 4 700 mg L<sup>-1</sup> at pH 6.54 (Figure 6.3e). It was suspected that, as the S was present in the EW in a soluble form, it tended to remain soluble regardless of the solution pH. Barber (1984) and Tabatabai (2005) indicated that sorption of sulphate decreases with rising pH, due to the changes in surface charge of soil minerals. This may be the cause of the slight increase noted from pH 3.37 to 6.54.

The Mg concentration decreased from pH 1.44 to 6.22, but increased again at high pH, probably also a result of dissolution of Mg-containing compounds at low pH that were not soluble at the higher pH (Figure 6.3d). The concentrations of Pb in the EW reflected similar trends to the other metallic cations (Figure 6.3f). At the lowest solution pH (1.44) the concentration was 59.2 mg L<sup>-1</sup>, decreasing to 5.69 mg L<sup>-1</sup> at pH 3.37 and to < 0.60 mg L<sup>-1</sup> at the higher pH values.

### 6.3.8 Phosphorus sorption

It should be noted that the term sorption is used here as a generic term to describe a wide range of P-fixation mechanisms. As was the case for the PT the SS had P sorption characteristics described by an L-type curve (Sparks, 2003), at low adsorbate concentrations (Figure 6.4). The EW tended toward an H-type curve at low adsorbate concentrations (Sparks, 2003); this type of curve being an extreme form of the L-type (Essington, 2004). The sorption of P by the SS was described well by both the Langmuir and Freundlich models ( $R^2 = 0.985$  and  $0.990$ , respectively) up to a residual P concentration of 23.3 mg L<sup>-1</sup>. A sharp increase in P-sorption was measured at higher residual P concentrations (Figure 6.4), probably a result of precipitation reactions. The calculated maximum sorption of 455 mg kg<sup>-1</sup> was similar to the observed value of 432 mg kg<sup>-1</sup>, at a residual P concentration of 23.3 mg L<sup>-1</sup>.

A number of authors report on the high P-sorption capacity of various types of slags (Johansson, 1999; Johansson and Gustafsson, 2000; McDowell, 2004; Drizo *et al.*, 2006). Generally the P-removal mechanism has been attributed to the formation of Ca-P compounds such as hydroxyapatite (e.g. Johansson and Gustafsson, 2000). Kostura *et al.* (2005) suggested that the adsorption of dissolved P is controlled by the amount of Ca present on the slag surface.



**Figure 6.4** Phosphorus sorption isotherms for slag (SS) from the Samancor Mn-smelter and electro-winning waste (EW) from MMC.

In the case of the EW, both the Langmuir and Freundlich models also adequately described ( $R^2 = 0.996$  and  $0.995$ , respectively) the sorption of P over the entire P concentration range investigated. The calculated sorption maximum for the EW ( $2\,500\text{ mg kg}^{-1}$ ) was slightly higher than the observed value of  $2290\text{ mg kg}^{-1}$ , at a residual P concentration of  $17.8\text{ mg L}^{-1}$ . It appeared that maximum sorption had not been achieved in the EW, reflected in the sorption isotherm (Figure 6.4). Sorption of P by oxide minerals, notably Fe and Al oxides is a well known phenomenon (Schwertmann and Taylor, 1989; Bastin *et al.*, 1999). However, it is doubtful that P-fixation by the EW was entirely due to sorption by the oxide minerals present in the waste, and various other P-removal mechanisms, such as precipitation reactions, may have played a role. Lindsay *et al.* (1989) and Sims and Piersynski (2005) suggested that in the soil environment, under certain conditions, added phosphate (as fertilisers) may precipitate with other soil constituents to form various P-minerals. In the case of the EW the high amounts of soluble Ca, Mg, Mn and  $\text{NH}_4^+$  may have resulted in the formation of new P-minerals, removing large amounts of P from solution.

The same procedure used to determine the amount of P sorbed to achieve residual P concentrations of  $0.05$  and  $0.20\text{ mg L}^{-1}$  for the PT (Section 4.2.2.6) was used for the SS and

EW (Table 6.7). The estimated concentrations of P sorbed by the SS to achieve residual P concentrations of 0.05 and 0.20 mg L<sup>-1</sup> were lower than the calculated concentration (Table 6.7). In the case of the EW the estimated values were higher than the calculated values (Table 6.7). These discrepancies found between the estimated and calculated amounts of P sorbed to achieve the desired residual concentrations may be explained by considering the basic assumptions of the Langmuir model.

As the Langmuir model was originally developed for gaseous systems, a number of assumptions are made and these may not hold true in more complex systems, such as soil (or waste) (Essington, 2004). The model assumes, *inter alia*, that all the binding sites or locations share the same binding energy and that sorption only occurs at these specific sites, with maximum sorption occurring when all these binding sites are filled (forming a monolayer of adsorbate) (Sparks, 2003; Essington, 2004). Furthermore, the model assumes that there are no reactions between adsorbed species and that equilibrium conditions are attained. It is unlikely that these assumptions will hold true for the different types of waste.

**Table 6.7**            The amount of P sorbed by slag (SS) from the Samancor Mn-smelter and electro-winning waste (EW) from MMC to achieve residual P concentrations of 0.05 and 0.20 mg L<sup>-1</sup>. The ‘estimated’ value was estimated from the isotherm plot (Figure 6.4), and the ‘calculated’ value was determined using the linear form of the Langmuir isotherm

Sample	Determination	Amount of P sorbed (mg kg <sup>-1</sup> ) to achieve the residual P values (mg L <sup>-1</sup> ) indicated	
		0.05 <sup>†</sup>	0.20 <sup>‡</sup>
SS	Estimated	14.5	58.1
	Calculated	21.1	89.3
EW	Estimated	226	647
	Calculated	125	500

†      Zupancic (1996).  
‡      Fox and Kamprath (1970).

In the SS, the model overestimated the amount of P sorbed to achieve the desired residual P concentrations. It is hypothesized that, at the low adsorbate concentrations, loss of P was due to adsorption onto exchange sites of the SS (and so probably behaving according to the assumptions of the model). At the higher adsorbate concentrations other mechanisms may have led to an increase in the loss of P from solution. As the model was derived from the

entire sorption range and does not differentiate between multiple fixation mechanisms, the different mechanisms may not have been adequately accounted for (i.e., multi-site or multi-mechanism P fixation in the SS), and so the application of the model led to an overestimation of the P requirement at the low adsorbate concentrations. In the EW, where the Langmuir model underestimated the amount of P sorbed to achieve the desired residual P concentrations, it is likely that most of the P was lost due to complexation and precipitation with free salts present in the solution, rather than by actual adsorption mechanisms onto solid phases. This may have been the cause of the increased loss of P from the solution, even at the low adsorbate concentrations, suggesting that the model was describing precipitation reactions rather than the surface sorption mechanisms for which it was originally intended.

Nonetheless, in both the wastes, the model does not adequately predict the P-sorption capacity at very low residual P concentrations, as it does not account for multiple mechanisms of P loss. Sparks (2003) indicated that, in pure or ideal systems, the Langmuir model can describe both sorption and precipitation reactions, but not as a single model (as used here) and, perhaps, other models may be better suited (e.g. two-surface Langmuir model) to describe multi-site sorption, or possibly, precipitation reactions (Sparks 2003; Essington, 2004).

## 6.4 Conclusions

While both the SS and EW are waste by-products from the production of Mn-metal, it is clear that they have dramatically different chemical characteristics. The SS is a highly alkaline material, exhibiting moderately high potential as a liming agent. It is easily weathered under acidic conditions with the release of large amounts of Mn, along with basic cations (Ca and Mg). The land disposal of the slag may be feasible if acidity from the soil does not promote excessively high rates of dissolution that could release high amounts of Mn, especially if applied at high rates. If dissolution of the SS in the soil environment is moderately slow, depending on the soil characteristics, it is likely that the release of metals will be buffered in the soil system. The primary element of concern in the SS is Mn. It is a common soil element and an essential plant nutrient. Given the moderately high alkalising power of the SS and the likely rates of dissolution in the soil environment, Mn is unlikely to be a major concern from a toxicity point of view. Probably of more immediate concern

is the high P-fixation capacity of the SS. The rate of P desorption from the SS is not known and high application rates may lead to P deficiencies in plants. In addition, high rates of SS application to a soil may result in excessively high pH, this possibly leading to nutrient deficiencies.

Unlike the SS, the EW has high concentrations of readily soluble elements, notably Mg, Mn, N and S, as well as Co and Ca. These are all plant essential nutrients, suggesting potential as a fertiliser. The waste has a high EC that may lead to salinity problems if applied at high rates to land. The high solubility of these salts also indicates potential toxicity concerns if the waste is to be land-applied. The application rate at which this may be cause for concern is dependent on the ability of a receiving soil to buffer the effects of applying the waste to that soil. In addition, the EW also has a high P-fixation capacity that may result in P deficiencies.

Based on the results of the TCLP and acid rain extractions, both wastes are considered hazardous and present a high risk to the surrounding environment, notably water resources. Given that currently both wastes are disposed of at 'dedicated' disposal sites, the amount of potentially toxic elements released, based on the above-mentioned extractants, may be very high. This may result in severe point-source pollution if adequate measures are not taken to curb the dispersal of pollutants to the surrounding environment. However, in terms of land disposal, the waste is to be diluted within a soil matrix, reducing this potential risk. Furthermore the soil may be beneficial in assimilating the waste, rendering it harmless to the environment. Subsequent investigations were conducted to examine the affect of applying either EW or SS on soil chemical properties of six different soils and the effect on the growth of ryegrass grown in waste-treated soils.

## CHAPTER 7

### EFFECT OF MANGANESE-RICH PROCESSING WASTES ON SOME CHEMICAL PROPERTIES OF SIX SOILS

#### 7.1 Introduction

The potential of soils to assimilate various pollutants depends on the specific attributes of that soil. One of the most important parameters of the soil-waste system driving the release and behaviour of many elements is pH (Yan *et al.*, 2000). Neutralisation reactions are the first response of the soil system to the addition of basic or acidic waste (Overcash and Pal, 1979). If the soil's buffering capacity is exceeded (such as when excessively high rates of waste are applied) then the soil system will tend towards the pH of the added waste, which may result in changes in the soil's assimilative capacity (Overcash and Pal, 1979). The ability of a soil to buffer these changes depends on a variety of factors related to specific soil properties (e.g. mineralogy, texture, organic matter; Bloom, 2000).

The addition of saline wastes to soil can result in changes in the EC of the soil and possibly lead to soil salinity. Soil salinity is a condition that can limit the ability of plants to absorb water from the soil solution (osmotic imbalance), lead to phytotoxic conditions for plants, or alter the physical or chemical properties so that long-term detrimental effects reduce productivity or vegetation establishment (Essington, 2004). Overcash and Pal (1979) indicate that ionic interferences may also occur, where competition between ions limits nutrient uptake by plants. The ability of a soil to assimilate waste-applied salts varies depending on specific soil properties, but also depends on water movement in the soil and vegetation grown in that soil. Again, if excess salt is added to a soil then the assimilative capacity of soil may be exceeded and a saline condition may result.

The primary aims of this investigation were to determine:

- the effect of adding SS or EW on the pH and EC of six soils of varying properties;
- the change in exchangeable acidity of the six soils after treatment with SS or EW; and
- in the case of the EW-treated soils, the change in  $\text{NH}_4^+$ -N concentrations over time.

These parameters were assessed using an incubation experiment. This allowed for the control of soil moisture and temperature, whilst maintaining an homogenised soil:waste mixture under aerobic conditions. While this type of control was favourable, it did disregard the influence of leaching of soluble salts and products of reactions that formed in the soil. In this sense the incubation experiment can be regarded as a situation where the waste is restricted to the upper layer of the soil system and there are no losses by leaching.

## 7.2 Materials and methods

### 7.2.1 Waste and soil collection and preparation

The SS and EW described in Chapter 6 were used in this investigation.

The six soils collected for use in the incubation experiment were the A horizons of a Bonheim (Bo), Hutton (Hu), Inanda (Ia), Shortlands (Sd) and Valsrivier (Va) soil forms and the E horizon of a Longlands (Lo) soil form (Table 7.1). The selected horizons were excavated, from previously opened pits, by shovel, placed in 50 kg nylon bags and transported to the University for further handling. Each soil was air-dried, milled to pass through a 2 mm sieve and thoroughly mixed. Sub-samples of the six soils were sent to the Soil Fertility and Analytical Services Division (KwaZulu-Natal Department of Agriculture, Cedara) for fertility analysis. In addition, pH (water and 1 M KCl), EC, CEC, OC, total N and particle size were determined for each of the soils using methods described in Chapter 4.

### 7.2.2 Incubation experiment

#### *7.2.2.1 Experiment design*

The SS was mixed with each of the soils at rates of 30, 60, 120, 240 and 480 g kg<sup>-1</sup>, and the EW was mixed at rates of 20, 40, 80, 160 and 320 g kg<sup>-1</sup>. For each soil type, an unamended treatment was included (control). As part of the objective of the study was to determine upper limits for land application of these wastes, the application rates were selected to extend from low to very high rates. The equivalent 'field' application rates for the SS were from 72 to 1 152 Mg ha<sup>-1</sup> for the 30 to 480 g kg<sup>-1</sup> treatments, respectively, and 48 to 768



Mg ha<sup>-1</sup> for the 20 to 320 g kg<sup>-1</sup> EW treatments, respectively (calculated using an assumed soil bulk density of 1.2 g cm<sup>-3</sup> and an incorporation depth of 200 mm). After thorough mixing of soil:waste mixtures, they were moistened to field capacity. This was achieved by adding the required amount of distilled water to the containers and allowing them to equilibrate for a few hours before gently remixing the samples. Field capacity was considered to be the water content of the soils and soil:waste mixtures at a matric potential of -30 kPa. This was previously determined on the soils and mixtures using standard pressure pot and plate apparatus (Moodley, 2001). The mixtures (2.1 kg of soil or soil:waste mixture) were placed in plastic bags and stored in dark plastic buckets at a constant 24 °C. To prevent anaerobic conditions developing, the buckets and bags were opened once a week and the mixtures and soils thoroughly mixed. The experiment was unreplicated, partly due to analytical constraints, but primarily because the investigation was aimed at elucidating the trends. Unfortunately this did not allow for the use of statistical analysis to compare results.

**Table 7.1** Description of soil forms, sampling location and current land use of the six soils used in the incubation experiment

Soil form <sup>†</sup>	Horizon used	Soil form description <sup>†</sup>			Sampling location	Land use
		Topsoil	-----Subsoil-----			
<b>Bonheim</b>	A	melanic	pedocutanic B	unspecified	Ukulinga Research Farm, Pietermaritzburg	undisturbed grassland on upland, level, plateau
<b>Hutton</b>	A	orthic	red apedal B	unspecified	Brookdales Farm, Howick	old maize/soya lands, fallow ± 5 years
<b>Inanda</b>	A	humic	red apedal B	unspecified	Worlds View, Hilton	forestry
<b>Longlands</b>	E	orthic	E horizon	soft plinthic B	South African Sugar Association, Mt Edgecombe	previously sugarcane, grassland for ± 12 years
<b>Shortlands</b>	A	orthic	red structured B	-	Hesketh Drive Conservancy, Pietermaritzburg	undisturbed grassland
<b>Valsrivier</b>	A	orthic	pedocutanic B	unconsolidated material without signs of wetness	Muden, KwaZulu-Natal	sugarcane

<sup>†</sup> Soil Classification Working Group (1991).

#### 7.2.2.2 *Sampling and analysis*

The mixtures and soils were sampled after 3, 7, 14, 21, 28, 42, 56, 70, 84, 112, 140, 196 and 252 days. The initial dry mixtures were considered as time zero (Day 0). At each sampling time enough material was removed to give the equivalent of about 100 g air-dry material (calculated from the predetermined moisture content). The sub-samples were immediately air-dried and milled (< 2 mm) for analysis. Not all analyses were conducted on all samples due to limited sample size and practical considerations.

The pH (water and 1 M KCl) and EC were determined at all sampling dates. Exchangeable acidity (Sims, 1996) was determined for selected sampling dates (Days 0, 28, 84, 140 and 252). Considering that the EW had high concentrations of soluble  $\text{NH}_4^+$  it was considered necessary to determine the loss of this form of N when incubated with the different soils. As such,  $\text{NH}_4^+$  concentrations in the EW treated soils were determined for selected sampling dates (Days 0, 70, 196 and 252) by the distillation procedure (Bremner and Mulvaney, 1982). All analyses were performed in duplicate and mean values are reported.

### 7.3 Results and discussion

#### 7.3.1 Soil properties

The pH of the soils ranged from acidic to neutral (Table 7.2). Generally all the soils had low amounts of exchangeable acidity, except for the Ia. The fertility analysis showed that there was also a wide range in the concentrations of plant nutrients (notably N, Ca, Mg and K). The Bo and Sd soils had the highest amounts of extractable Ca and Mg. The Ia soil had a high total N concentration, probably a function of the high OC content of this soil (Table 7.2) Particle size analysis showed that there was a wide range of soil textures, a favourable factor for the purposes of this investigation.

**Table 7.2** Physical and chemical properties of the six soils used in the incubation study

Parameter		Soil form <sup>†</sup>					
		Bo	Hu	Ia	Lo	Sd	Va
pH	H <sub>2</sub> O	6.47	5.34	4.30	6.05	6.04	7.01
	1 M KCl	5.12	4.57	4.00	4.90	4.94	5.89
Electrical conductivity (mS m <sup>-1</sup> )		27.0	17.0	5.42	4.00	9.00	8.70
Organic carbon (g 100g <sup>-1</sup> )		3.60	3.44	9.60	0.14	3.29	0.46
Total N (mg kg <sup>-1</sup> )		2276	2098	5121	533	2062	996
Extractable base cations <sup>‡</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	Ca	10.2	6.63	0.85	2.06	9.16	5.40
	Mg	7.17	3.04	0.20	0.62	4.88	3.35
	K	0.30	0.47	0.17	0.10	0.37	0.79
Exchangeable acidity (cmol <sub>c</sub> kg <sup>-1</sup> ) <sup>‡</sup>		0.08	0.21	4.71	0.03	0.05	0.06
Sum of cations (cmol <sub>c</sub> kg <sup>-1</sup> ) <sup>‡</sup>		17.8	10.4	5.92	2.80	14.5	9.60
Acid saturation (%) <sup>‡</sup>		bd	2.00	80.0	1.00	bd	1.00
Cation exchange capacity (cmol <sub>c</sub> kg <sup>-1</sup> )		23.8	12.7	13.0	2.54	14.0	13.0
Extractable metal cations <sup>‡</sup> (mg kg <sup>-1</sup> )	Mn	51.0	131	16.0	23.7	117	18.9
	Cu	8.94	11.6	4.40	2.23	15.1	3.20
	Zn	5.48	7.47	2.00	1.76	3.30	4.84
Extractable P (mg kg <sup>-1</sup> ) <sup>‡</sup>		4.81	10.1	20.0	4.05	2.91	8.20
<b>Particle size (%)</b>							
Coarse sand (0.50–2 mm)		3.5	4.2	3.9	1.8	2.9	4.6
Medium sand (0.25–0.5 mm)		3.2	1.0	5.7	27.3	1.9	7.3
Fine sand (0.053–0.25 mm)		13.1	6.4	26.3	47.5	7.2	43.3
Silt (0.002–0.053 mm)		50.1	34.3	42.2	12.8	45.6	18.7
Clay (<0.002 mm)		30.1	54.0	21.9	10.6	42.4	26.1

bd below detection.

† Bo – Bonheim A, Hu – Hutton A, Ia – Inanda A, Lo – Longlands E, Va – Valsrivier A, Sd – Shortlands A.

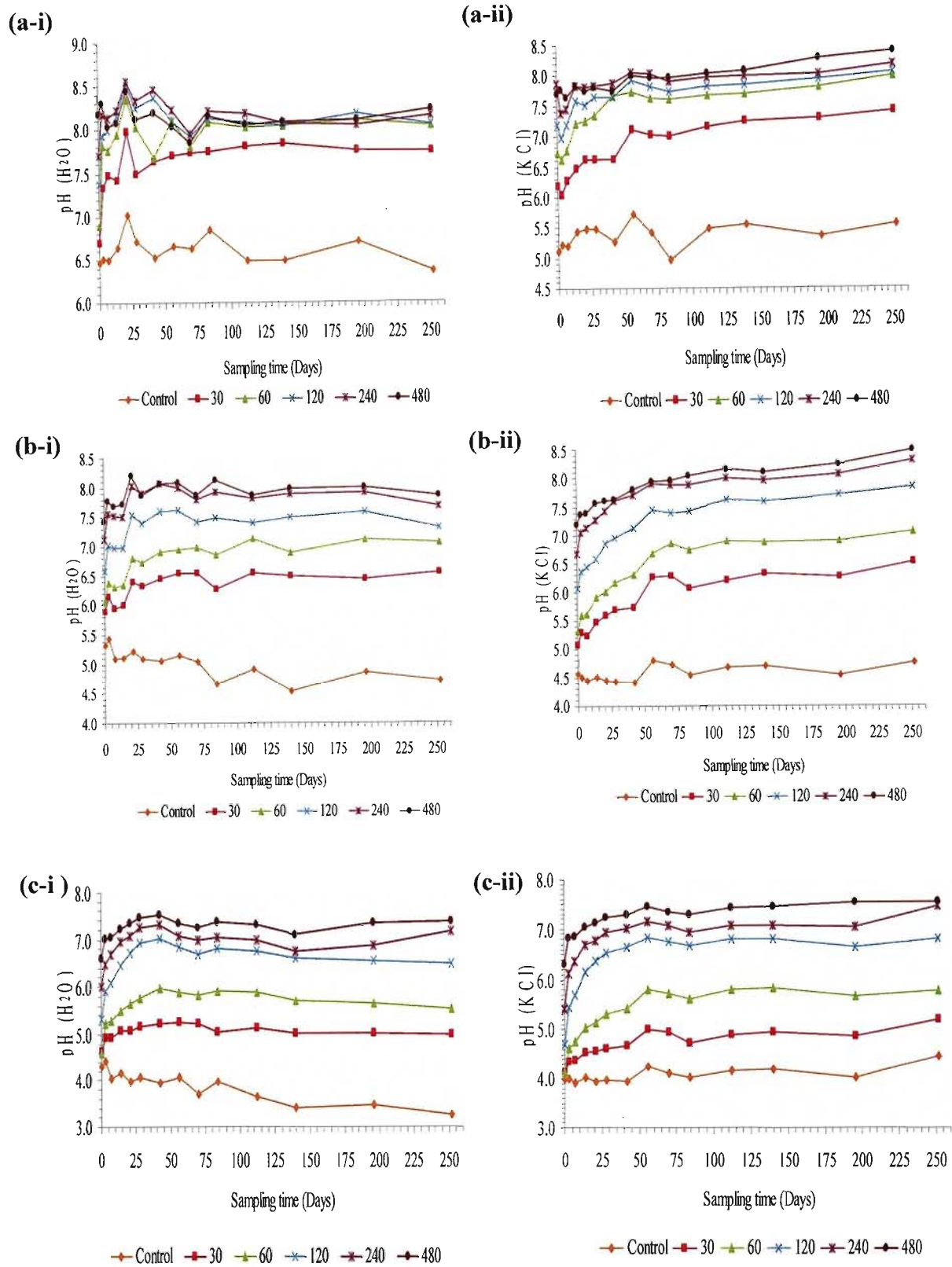
‡ Analysis conducted by the Soil Fertility and Analytical Services Division (KwaZulu-Natal Department of Agriculture, Cedara).

### 7.3.2 Incubation experiment

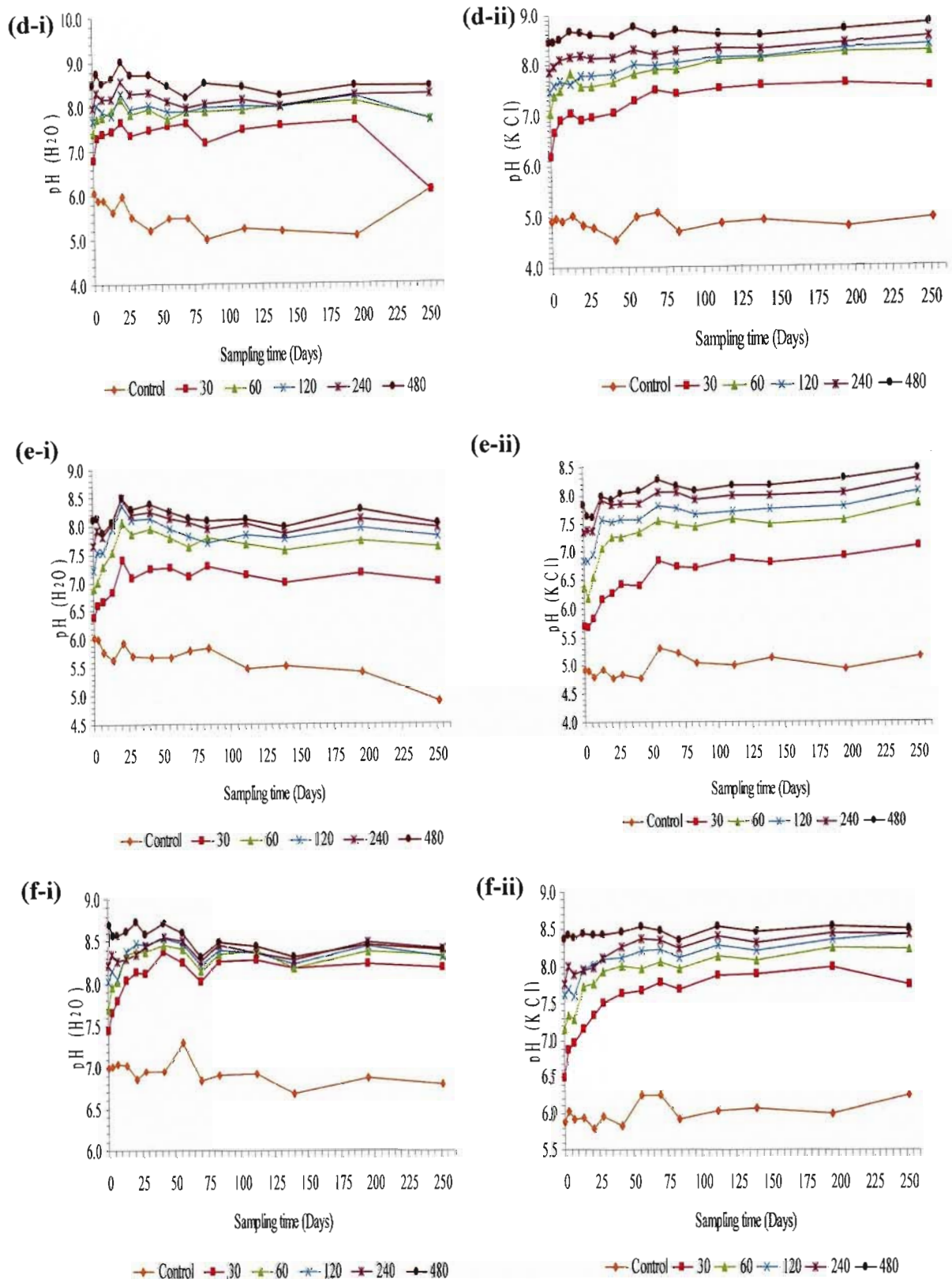
#### 7.3.2.1 Effect of slag

##### 7.3.2.1.1 pH and exchangeable acidity

The pH of all the soils increased with increasing application rate of SS (Figure 7.1).



**Figure 7.1** The change in (i) pH<sub>water</sub> and (ii) pH<sub>KCl</sub>, over time, of incubated (a) Bonheim, (b) Hutton, (c) Inanda, (d) Longlands, (e) Shortlands and (f) Valsrivier soils after the addition of slag from the Samancor Mn-smelter at rates of 0 (control), 30, 60, 120, 240 and 480 g kg<sup>-1</sup>.



**Figure 7.1 (contd)** The change in (i) pH<sub>water</sub> and (ii) pH<sub>KCl</sub>, over time, of incubated (a) Bonheim, (b) Hutton, (c) Inanda, (d) Longlands, (e) Shortlands and (f) Valsrivier soils after the addition of slag from the Samancor Mn-smelter at rates of 0 (control), 30, 60, 120, 240 and 480 g kg<sup>-1</sup>.

Generally, the increase was observed in the first 21 to 28 days, depending on the soil type. Thereafter pH values remained relatively constant. In most of the soils, the application of SS resulted in alkaline soil conditions regardless of the application rate, though there were exceptions.

In the Ia soil (Figure 7.1c) at an SS application rate of  $120 \text{ g kg}^{-1}$  the equilibrium pH was near-neutral, but remained slightly acidic at the lower SS application rates ( $30$  and  $60 \text{ g kg}^{-1}$ ). A similar situation was observed for the Hu soil (Figure 7.1b), though the pH values measured were higher than in the Ia soil. In some of the soils (Bo, Lo and Va) the effect of the high application rate of SS ( $480 \text{ g kg}^{-1}$ ) was immediate and changed little over the duration of the experiment. Apart from in the Ia and Hu soils, the pH of the soils with high SS application rates ( $120$ ,  $240$  and  $480 \text{ g kg}^{-1}$ ) tended to be similar once the apparent equilibrium state had been reached. This trend was only noted at the two highest SS application rates in the Ia and Hu soils. This was attributed to the higher acidity of these two soils when compared to the others (see Section 7.3.2.3).

It was noted that the  $\text{pH}_{\text{water}}$  showed a high degree of variability over time, relative to the buffered  $\text{pH}_{\text{KCl}}$  values. This was attributed to effects of atmospheric carbon dioxide on the  $\text{pH}_{\text{water}}$ , where the  $\text{pH}_{\text{KCl}}$  could better buffer against this influence. A similar effect was reported by Buyeye (2005) in a similar experiment.

The change in the exchangeable acidity of all the soils, except the Ia soil, tended to be variable after the addition of SS at Day 0 (Table 7.3), reflecting sample variability rather than the effect of the SS. The lack of replication in the incubation experiment did not permit for analysis of this variance, and as such, is only speculated on. As the exchangeable acidities of the control soils were generally low, except for the Ia soil, the effect of adding SS was not marked. By Day 252 all SS-treated soils had very low exchangeable acidities, most being below detection.

In the Ia soil the effect of the SS was more marked. As the control Ia soil had a considerably higher initial exchangeable acidity than the other soils, the change caused by the SS was more marked.

**Table 7.3** Exchangeable acidity ( $\text{cmol}_c \text{ kg}^{-1} \times 100$ ) in Bonheim, Hutton, Inanda, Longlands, Shortlands and Valsrivier soils, at selected sampling times, after incubation with slag from the Samancor Mn-smelter at rates of 0, 30, 60, 120, 240 and 480  $\text{g kg}^{-1}$

Soil	Application rate ( $\text{g kg}^{-1}$ )	Sampling day				
		0	28	84	140	252
Bonheim	0	9.58	16.6	14.1	10.8	4.09
	30	3.83	7.31	0.47	4.79	0.23
	60	2.87	3.33	3.30	4.19	bd
	120	3.83	2.00	8.02	7.19	bd
	240	2.87	7.32	10.4	10.8	bd
	480	3.83	8.65	10.4	12.0	bd
Hutton	0	20.1	27.3	23.1	26.9	25.86
	30	9.58	14.0	7.08	9.58	1.85
	60	5.75	14.0	1.89	7.78	0.46
	120	2.87	9.98	9.90	7.19	1.39
	240	1.91	4.65	8.02	9.58	bd
	480	4.79	5.99	12.7	15.0	bd
Inanda	0	264	400	346	347	426
	30	217	65.9	33.0	31.7	18.4
	60	199	23.3	17.5	19.2	7.65
	120	74.2	23.3	23.1	20.4	7.43
	240	19.6	25.9	22.2	19.2	5.63
	480	6.70	25.9	29.7	17.4	3.83
Longlands	0	11.5	12.6	9.43	7.18	7.50
	30	4.31	7.32	bd	2.99	bd
	60	0.96	1.99	0.47	1.80	bd
	120	0.48	5.98	3.30	5.98	bd
	240	2.39	3.33	3.77	5.99	bd
	480	4.31	4.66	4.72	8.38	bd
Shortlands	0	9.57	12.6	8.96	13.2	7.15
	30	2.39	8.65	1.41	4.19	0.69
	60	0.96	2.00	1.89	4.79	bd
	120	0.96	1.99	6.13	4.79	bd
	240	2.39	2.00	7.54	7.19	bd
	480	4.79	8.65	8.49	8.98	bd
Valsrivier	0	0.48	9.98	2.36	4.79	bd
	30	bd	0.00	bd	2.40	0.45
	60	0.48	0.66	1.41	1.80	bd
	120	0.96	1.99	4.24	5.39	bd
	240	2.39	4.65	6.13	5.39	bd
	480	3.83	4.66	10.4	5.99	bd

bd below detection.

The exchangeable acidity of the Ia control soil increased over time indicating that it had acid-generating potential, probably due to the oxidation of organic matter in the soil over time. At Day 0 the exchangeable acidity of the Ia soil decreased sharply as SS application rates increased. At SS application rates of 30, 60 and 120 g kg<sup>-1</sup>, in the Ia soil, the exchangeable acidity increased slightly from Day 0 to Day 28, but then tended to decrease thereafter. At a SS application rate of 480 g kg<sup>-1</sup> the exchangeable acidity of the Ia soil increased sharply from Day 0 to Day 28, and remained constant up to Day 84 decreasing again thereafter. The exchangeable acidity of the 240 g kg<sup>-1</sup> treatment remained relatively constant up to Day 140 but decreased sharply at Day 252.

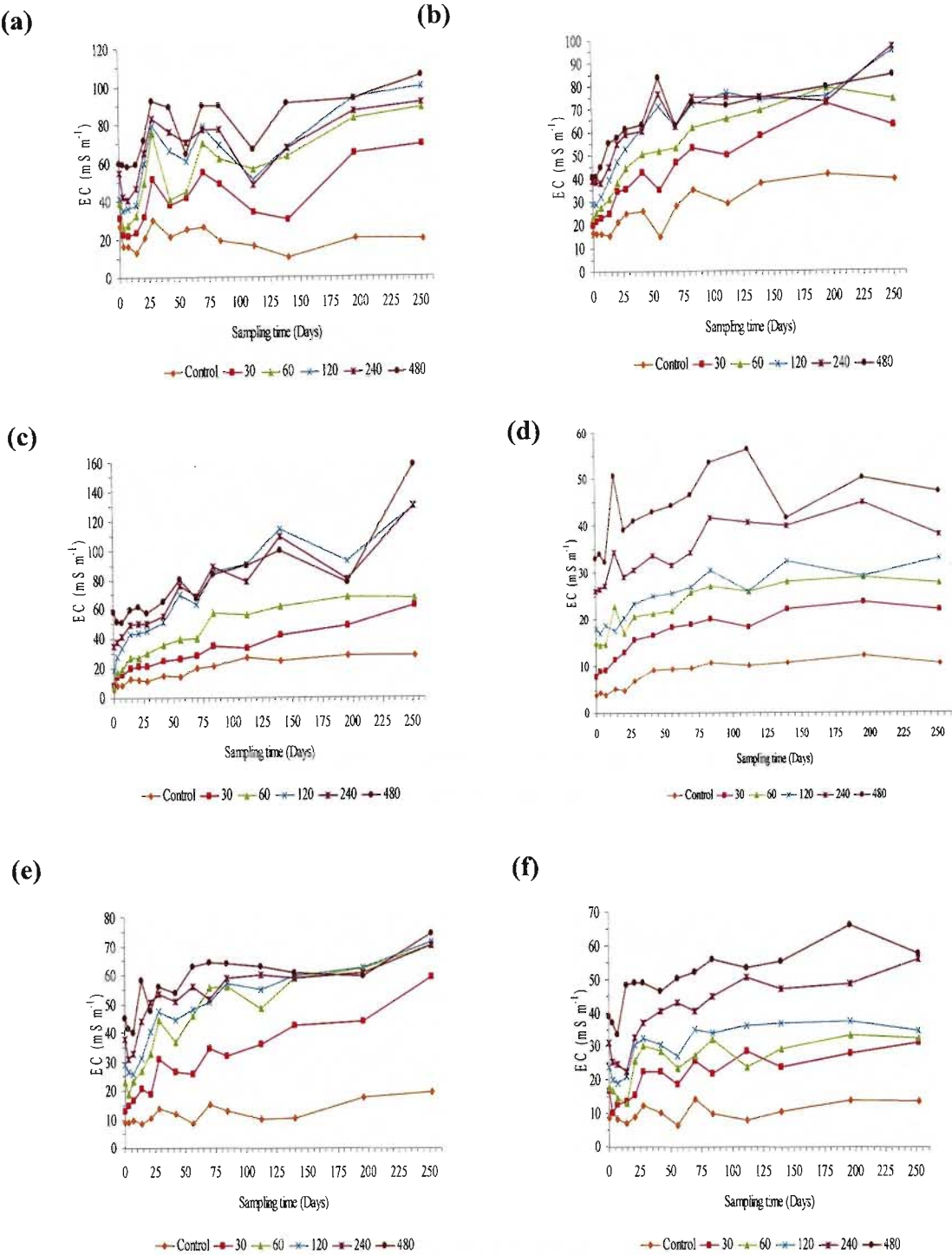
The alkalising potential of various slags have been recognised by some authors (Barber, 1984; Yan *et al.*, 1998; Yan *et al.*, 2000; Haynes, 2001). The increase in pH, after the addition of SS, was not unexpected considering the inherently high pH of the waste (Chapter 6). The short-term (up to about Day 28) increase in pH is attributed to rapid hydrolysis reactions, where H<sup>+</sup> ions are consumed in the dissolution of the silicate mineral(s) and the hydrolysis of CaO. This is, in part, supported by the decrease in exchangeable acidity for some of the soils.

#### 7.3.2.1.2 *Electrical conductivity*

Generally, the EC of the soils increased with increasing rates of SS addition, though values were all below 100 mS m<sup>-1</sup> (Figure 7.2). In some instances the EC decreased in the first few days and then increased sharply thereafter (e.g. Bo, Sd and Va soils; Figures 7.2a, e and f, respectively). In the Ia, Hu and Lo soils (Figures 7.2b, c and d, respectively) EC increased immediately from Day 0. After about 14 days there was a gradual increase in the EC of all the SS-treated soils. The EC values of some of the control soils also increased with time, indicating that there was an increase in salt concentrations in the soils, possibly due to decomposition of organic material and solubilisation of various soil components.

The EC of the untreated soils was generally low, as was the EC of the SS. However, for all soils, except the Lo and Va, the EC of the soils treated with high rates of SS tended to be higher than their expected combined influence. This suggested that there was an almost immediate release of ions in the mixtures resulting in the elevated EC values, though the mechanism is not clear.





**Figure 7.2** The change in electrical conductivity (EC), over time, of incubated (a) Bonheim, (b) Hutton, (c) Inanda, (d) Longlands, (e) Shortlands and (f) Valsrivier soils after the addition of slag from the Samancor Mn-smelter at rates of 0 (control), 30, 60, 120, 240 and 480  $\text{g kg}^{-1}$ .

It was speculated that in the Bo, Hu, Ia and Sd soils, which all had OC contents over 3 g 100 g<sup>-1</sup>, the effect of organic acids may have promoted the released ions from the SS. In the Lo and Va soils, with negligible OC contents, there may have been limited interaction between soil OC and the SS, thus this effect was not clearly observed. The general increase in EC over time supports the notion that the SS was undergoing dissolution, releasing cations bound in the mineral structures.

### 7.3.2.1.3 *Disposal limits*

To assess the likely rates at which the SS can be applied to land the pH<sub>water</sub> measured for SS-treated soils from Day 0 (initial effect) and 252 ('equilibrium state') were compared to predetermined pH values and the application rate (estimated field application rate determined from the rates used in the incubation experiments; Section 7.2.2.1) at which the desired pH was achieved are reported. In this instance two pH values were selected. A pH of 6.5 was chosen to represent an ideal soil pH for agricultural purposes (Table 7.4). A pH of > 8.0 was selected to highlight the SS application rate that resulted in the soils exhibiting the "plateau effect", described in Chapter 5 (Table 7.4). The other variables measured (EC and exchangeable acidity) were not considered to be a major concern in the SS thus are thus not used in this assessment.

The maximum SS-application rate at which a pH<sub>water</sub> of about 6.5 was achieved varied markedly between soils and appeared to be related to the initial pH of the soil. In very acidic soils (e.g. Ia) the maximum rate of 1152 Mg ha<sup>-1</sup> can be applied initially, though the evidence here indicates this will decrease over time to about 288 Mg ha<sup>-1</sup>. In slightly acidic soils (e.g. Lo and Sd) only the lowest application rates can be considered (< 72 Mg ha<sup>-1</sup>), while neutral soils will not benefit from the liming ability of the SS.

The application rate at which the pH was > 8.0 also varied for the different soil types and again appeared to be related to the initial soil pH. In the more acidic soils the pH threshold was not exceeded, even at the highest SS application rate (1152 Mg ha<sup>-1</sup>). In less acidic soils the maximum rate tended to result in the pH exceeding 8.0.

**Table 7.4** The equivalent field application rates of slag at which the pH of the six soils were about 6.5 and > 8.0 for Day 0 and Day 252. The rate used in the laboratory investigations are given in parentheses (g kg<sup>-1</sup>)

Sample day	Selection Criteria			
	pH ≈ 6.5		pH > 8.0	
	0	252	0	252
Soil type	Application rate (Mg ha <sup>-1</sup> )			
Bonheim	0 (0)	0	1152 (480)	144 (60)
Hutton	288 (120)	72 (30)	- <sup>†</sup>	-
Inanda	1152 (480)	120	-	-
Longlands	72 (30)	72 (30)	1152 (480)	240
Shortlands	72 (30)	72 (30)	1152 (480)	1152 (480)
Valsrivier	0	0	288 (120)	72 (30)

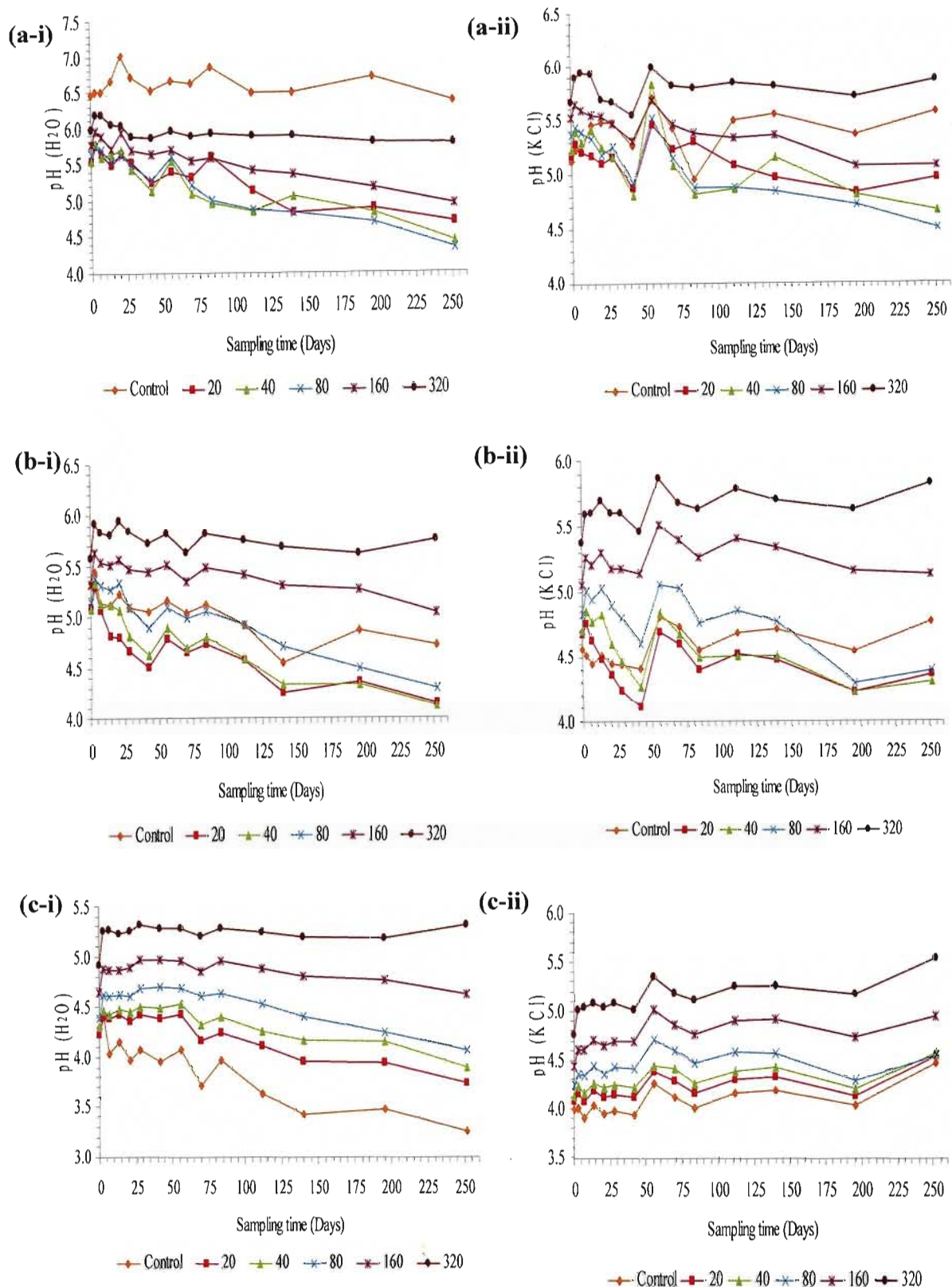
<sup>†</sup> The threshold pH value did not exceed 8.0, even at the highest slag application rate.

7.3.2.2 *Effect of electro-winning waste*

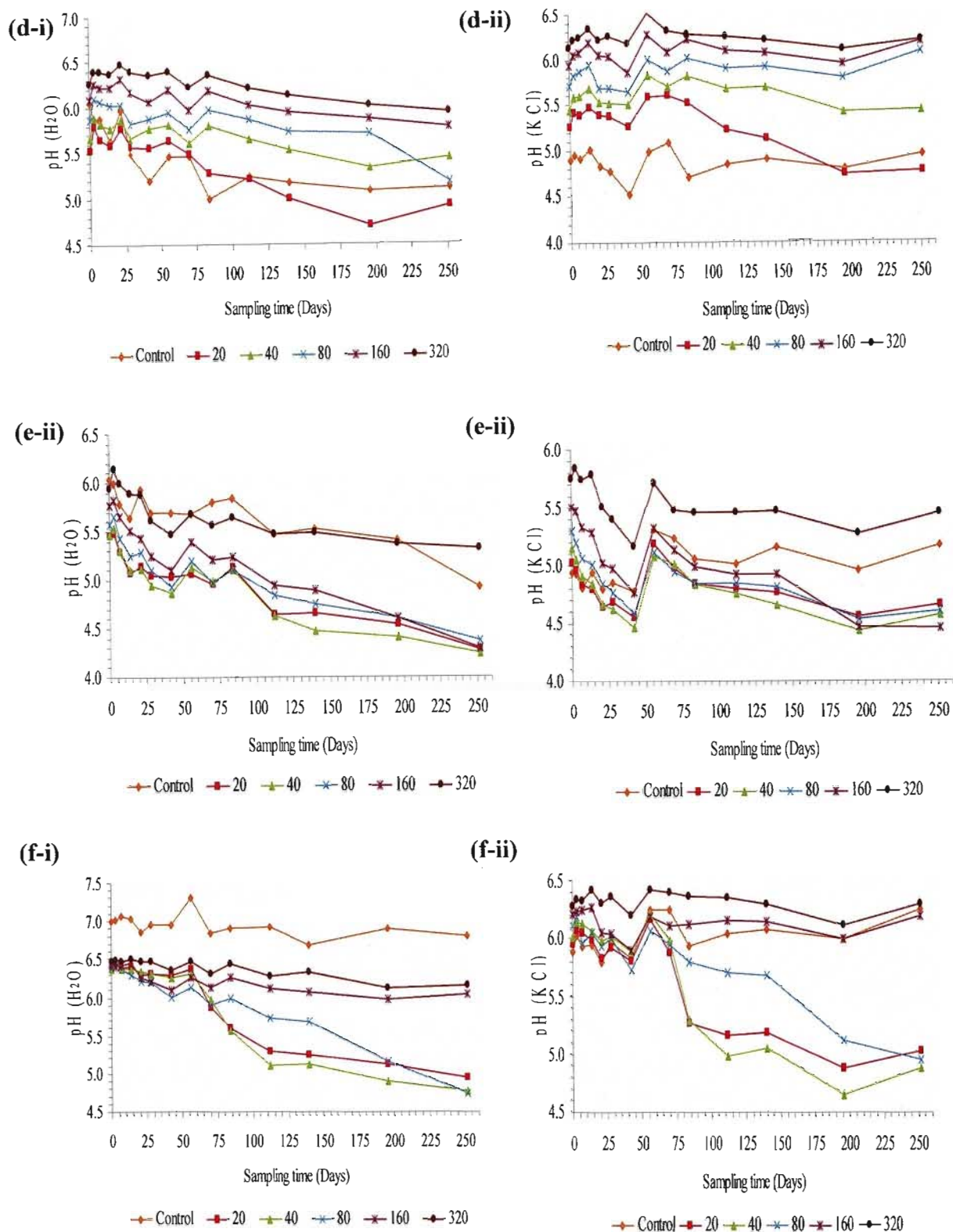
7.3.2.2.1 *pH and exchangeable acidity*

The addition of EW to the soils tended to decrease pH in the Bo, Sd and Va soils and increase it in the Hu, Ia and Lo soils (Figure 7.3), though this varied slightly depending on EW application rate, soil type and whether the pH was measured in water or KCl. For instance, in the Bo soil (Figure 7.3a) the pH<sub>water</sub> of the EW treatments were all lower than the control, but the pH<sub>KCl</sub> of the highest EW application rate was greater than that of the control, while the lower application rates were similar or lower than the control. A similar situation was noted for the Sd soil (Figure 7.3e). The pH (both water and KCl) of the Hu soil (Figure 7.3b) treated with 160 and 320 g kg<sup>-1</sup> EW was higher than the pH of control treatment, while the pH of the 20, 40 and 80 g kg<sup>-1</sup> treatments were similar to the control.

There tended to be sharp initial increase (from Day 0 to Day 3) in the pH of the Bo, Hu, Ia and Lo soils (Figures 7.3a, b, c and d, respectively) when treated with high rates of EW (typically > 80 g kg<sup>-1</sup>). This trend was only observed at the 320 g kg<sup>-1</sup> EW application rate in the Sd soil (Figure 7.3e) and was not evident in the Va soil (Figure 7.3f). Generally, the addition of EW to the soils resulted in a decrease in pH over time (after Day 3), this effect being more apparent in the pH<sub>water</sub> of the different soils. The pH of the soils treated with lower rates of EW (notably the 20, 40 and 80 g kg<sup>-1</sup>) decreased more sharply than the higher EW application rates. The pH values of the soils with high EW application rates (160 and 320 g kg<sup>-1</sup>) were generally more constant over time.



**Figure 7.3** The change in (i) pH<sub>water</sub> and (ii) pH<sub>KCl</sub>, over time, of incubated (a) Bonheim, (b) Hutton, (c) Inanda, (d) Longlands, (e) Shortlands and (f) Valsrivier soils after the addition of electro-winning waste from MMC at rates of 0 (control), 20, 40, 80, 160 and 320 g kg<sup>-1</sup>.

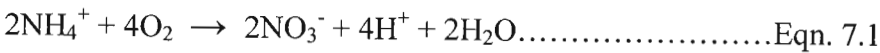


**Figure 7.3. (contd)** The change in (i) pH<sub>water</sub> and (ii) pH<sub>KCl</sub>, over time, of incubated (a) Bonheim, (b) Hutton, (c) Inanda, (d) Longlands, (e) Shortlands and (f) Valsrivier soils after the addition of electro-winning waste from MMC at rates of 0 (control), 20, 40, 80, 160 and 320 g kg<sup>-1</sup>.

The exchangeable acidity of most of the soils increased as EW application rates increased at Day 0, except in the Ia soil (Table 7.4). In this soil the addition of EW resulted in a decrease in the exchangeable acidity as application rate increased. This initial effect of the EW appears to reflect a dilution effect, where the change in the exchangeable acidity of the soil was increased or decreased relative to the initial exchangeable acidity of the soil. Generally, there was an increase in the exchangeable acidity of the EW-treated soils over time. For most soils, the most marked increases in exchangeable acidity over time were at the high EW application rates (160 and 320 g kg<sup>-1</sup>), where there was about a two to three-fold increase in exchangeable acidity from Day 0 to Day 28.

The increases at the lower EW application rates were more variable, but still indicated that some acidification was occurring due to the addition of the EW (reflected in the pH values; Section 7.3.2.1). The exchangeable acidity of most of the EW-treated soils continued to increase up to Day 84 before declining at Day 252 (though not in all cases e.g. Ia at 20, 40 and 80 g kg<sup>-1</sup>; and Hu at 20 and 40 g kg<sup>-1</sup>). There was a sharp decrease in exchangeable acidity of some treatments from Day 140 to 252.

The change in pH of the EW-treated soils was driven by the strong buffer capacity of the waste. The pure waste had a near-neutral pH (about 6.8; Chapter 6) and tended to drive the pH of the soils to around this value, especially at the higher application rates. This was particularly noticeable in the soils with low buffering capacity (e.g. Lo). The general decrease in pH over time was attributed primarily to the production of acidity by nitrification, whereby NH<sub>4</sub><sup>+</sup> is converted to NO<sub>3</sub><sup>-</sup>, releasing H<sup>+</sup> ions, by the following reaction (Bloom, 2000):



**7.3.2.2.2      *Electrical conductivity***

The addition of EW resulted in dramatic increases in the EC of the soils (Figure 7.5), with the EC values tending to double with the doubling of the EW application rate, for each soil type. This was expected considering the initially high EC of the EW and the generally low



EC of the soils. Generally, there was a decline in the EC of the EW-treated soils (except for the Lo soil) from Day 0 to about Day 21.

**Table 7.5** Exchangeable acidity ( $\text{cmol}_e \text{ kg}^{-1} \times 100$ ) in Bonheim, Hutton, Inanda, Longlands, Shortlands and Valsrivier soils, at selected sampling times, after incubation with electro-winning waste from MMC at rates of 0, 20, 40, 80, 160 and  $320 \text{ g kg}^{-1}$

Soil	Application rate ( $\text{g kg}^{-1}$ )	Sampling day				
		0	28	84	140	252
Bonheim	0	9.58	16.6	14.1	10.8	4.09
	20	11.0	16.6	8.49	12.6	6.14
	40	13.9	28.6	22.2	16.8	13.0
	80	22.0	43.3	43.9	34.1	22.5
	160	37.3	65.8	99.5	64.1	20.0
	320	59.9	143	191	130	28.9
Hutton	0	20.1	27.3	23.1	26.9	25.9
	20	23.5	37.9	58.5	52.1	71.6
	40	30.2	41.9	69.8	62.3	81.0
	80	38.3	68.5	82.5	62.3	50.1
	160	68.4	87.1	110	88.0	27.5
	320	54.6	162	155	131	41.1
Inanda	0	264	400	346	347	426
	20	185	253	247	244	305
	40	131	202	219	234	269
	80	107	154	166	172	256
	160	81.4	124	142	122	72.9
	320	99.5	175	175	149	41.9
Longlands	0	11.5	12.6	9.43	7.18	7.50
	20	11.5	18.0	22.16	18.6	10.5
	40	11.5	33.9	33.5	33.5	5.83
	80	18.7	48.6	47.6	43.1	6.06
	160	29.2	67.2	89.6	85.0	12.6
	320	50.3	104	142	108	23.6
Shortlands	0	9.57	12.6	8.96	13.2	7.15
	20	13.4	18.0	20.7	24.5	13.4
	40	17.2	23.3	34.4	29.3	21.0
	80	28.7	35.3	57.5	44.3	21.7
	160	46.0	77.8	81.6	73.1	45.0
	320	27.8	119	150	130	34.6
Valsrivier	0	0.48	9.98	2.36	4.79	bd
	20	9.10	23.3	22.2	13.8	5.85
	40	17.2	32.6	39.1	33.5	10.1
	80	24.4	51.2	67.4	47.3	17.3
	160	44.5	99.2	99.0	63.5	19.1
	320	68.0	148	176	147	31.1
bd	below detection.					

The EC of the EW-treated Lo soil (Figure 7.4d) increased from Day 0 to Day 3, before decreasing again. For most of the soils, equilibrium was reached after about 28 days, when the EC of the different soils tended to remain relatively constant.

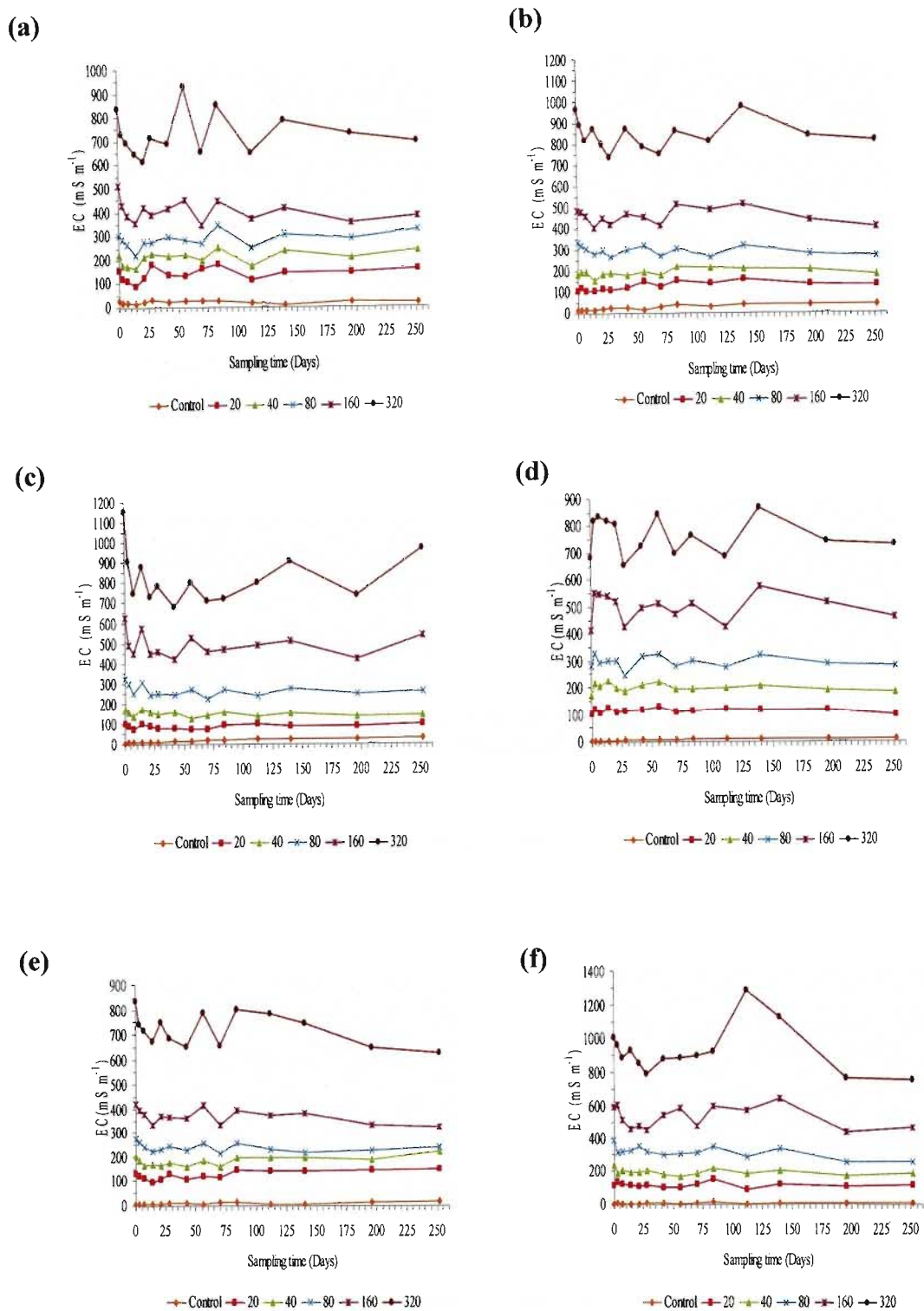
The high EC of the waste-treated soils is a clear indication that land disposal of the EW can result in severe salinity problems. At the lower application rates (20 and 40 g kg<sup>-1</sup>) the EC values of the soils were about 200 mS m<sup>-1</sup> and below, while the EC values were generally > 400 mS m<sup>-1</sup> at EW application rates of > 80 g kg<sup>-1</sup>, the EC values increasing exponentially up to the highest rate. At these high EW application rates the salinity exceeds thresholds set for classification of saline soils (> 400 mS m<sup>-1</sup>; see Section 6.3.3) and this may present problems for plant growth and leaching of the soluble component of the waste into groundwater. Thus a more conservative approach is adopted here with the recommendation to limit the application of EW to < 40 g kg<sup>-1</sup>.

#### 7.3.2.2.3 *Effect of EW on NH<sub>4</sub><sup>+</sup>-N concentrations*

The most notable effect of adding EW to the soils was to increase the concentrations of NH<sub>4</sub><sup>+</sup>-N in the soil, due to the high initial concentrations in the waste (Table 7.6). It may have been expected that the amount of NH<sub>4</sub><sup>+</sup>-N in the EW-treated soils would be relative to the amount in the EW, at least at the initial sampling date. In some cases this did not appear to hold true. For instance, in the Ia soil treated with 160 and 320 g kg<sup>-1</sup>, greater amounts of NH<sub>4</sub><sup>+</sup>-N were measured (2 230 and 3 970 mg kg<sup>-1</sup>, respectively) than the expected contribution from the EW applied (1 400 and 2 800 mg kg<sup>-1</sup>). Conversely, in the Lo soil the concentration of NH<sub>4</sub><sup>+</sup>-N measured (2 024 mg kg<sup>-1</sup>) at the highest rate of EW application was considerably lower than expected. On the whole, however, the amounts measured were relative to the contribution expected from the waste. Generally, NH<sub>4</sub><sup>+</sup>-N concentrations decreased over time, except at the high EW application rates (typically 160 and 320 g kg<sup>-1</sup>), where NH<sub>4</sub><sup>+</sup>-N concentrations tended to remain relatively constant or increase slightly.

Considering that the EW contained a high concentration of NH<sub>4</sub><sup>+</sup> it was expected that there would be an increase in acidity (and concomitant lowering of soil pH and loss of NH<sub>4</sub><sup>+</sup>-N). This was clear for the lower EW application rates in most of the soils, where along with a lower pH, the exchangeable acidity increased and concentrations of NH<sub>4</sub><sup>+</sup>-N decreased.





**Figure 7.4** The change in electrical conductivity (EC), over time, of incubated (a) Bonheim, (b) Hutton, (c) Inanda, (d) Longlands, (e) Shortlands and (f) Valsrivier soils after the addition of electro-winning waste from MMC at rates of 0 (control), 20, 40, 80, 160 and 320  $\text{g kg}^{-1}$ .

**Table 7.6** Ammonium-N ( $\text{mg kg}^{-1}$ ) in Bonheim, Hutton, Inanda, Longlands, Shortlands and Valsrivier soil, at selected sampling times, after incubation with electro-winning waste from MMC at rates of 0, 20, 40, 80, 160 and  $320 \text{ g kg}^{-1}$ .

Soil	Application rate ( $\text{g kg}^{-1}$ )	Sampling day			
		0	70	196	252
Bonheim	0	310	292	202	185
	20	383	351	181	190
	40	565	604	238	271
	80	933	1017	468	511
	160	1741	1785	1428	1408
	320	3081	3063	3016	2836
Hutton	0	284	278	219	186
	20	450	465	207	199
	40	606	555	428	429
	80	972	818	1016	1051
	160	1724	1829	1872	1818
	320	3722	3682	3683	3697
Inanda	0	451	469	431	454
	20	633	594	518	542
	40	793	783	773	762
	80	1293	1279	1215	1299
	160	2230	2308	2058	2085
	320	3974	3957	3407	3430
Longlands	0	44.2	55.7	54.7	30.9
	20	202	202	190	183
	40	403	412	414	411
	80	562	576	705	685
	160	1256	1268	1382	1373
	320	2024	2002	2453	2431
Shortlands	0	217	224	183	166
	20	323	348	178	216
	40	501	401	202	223
	80	740	697	621	642
	160	1231	1107	1446	1493
	320	2656	2735	2984	2938
Valsrivier	0	92.8	101	61.8	45.2
	20	284	213	183	54.6
	40	465	508	500	197
	80	895	915	863	499
	160	1455	1443	1861	1830
	320	3401	3458	3702	3745

At the high EW application rates there was still an increase in exchangeable acidity, but this was not associated with dramatic decreases in  $\text{NH}_4^+$ -N concentrations or marked

lowering of the pH. It is suspected that at the high EW application rates the system buffered well against these changes, controlled primarily by the high amount of EW in the soil.

At the low EW application rates (up to about 80 g kg<sup>-1</sup>), the N supplied by the EW may have enhanced microbial activity and increased the rate of transformation of NH<sub>4</sub><sup>+</sup>-N into other forms of N (increasing acidity). At the higher rates, microbial activity in the soil may have been suppressed so reducing the rate of nitrification of NH<sub>4</sub><sup>+</sup>-N to other forms of N. Tanyolaç *et al.* (2001) reported suppression of the growth rates of ‘mixed culture’ as they increased the concentration of NH<sub>4</sub><sup>+</sup> from 2.0 to 204 mM (as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), with maximum growth rate around 10.4 mM NH<sub>4</sub><sup>+</sup>. The concentration of NH<sub>4</sub><sup>+</sup> added by the EW ranged from about 12.6 to 201 mM kg<sup>-1</sup>, suggesting that at the higher application rates inhibition of microbial activity may have resulted. The high EC and metal toxicity (notably Mn) may also have reduced microbial activity.

#### 7.3.2.2.4 *Disposal limits*

A similar comparison was used to assess likely limits of disposal of the EW as was used for the SS (Section 7.3.2.1.3). However, in this instance the EC was used as the determining factor. The pH of the EW was considered favourable for plant growth (near-neutral) so was not considered to be a problem, and thus not a suitable indicator for disposal limits. While the NH<sub>4</sub><sup>+</sup> concentrations were high in some instances, the EC was considered a better overall indicator of the potential disposal limits. Two limits were selected for comparison. An EC of < 200 mS m<sup>-1</sup> was chosen to represent a relatively low level of salinity (Section 6.3.3), while an EC > 400 mS m<sup>-1</sup> was chosen to represent a saline soil condition and give an indication of the tendency towards the “plateau effect” (Chapter 5).

In almost all soils the amount of EW that could be applied without the EC exceeding 200 mS m<sup>-1</sup> was between 48 and 96 Mg ha<sup>-1</sup>, regardless of the sampling time (Table 7.7). The EW application rate that caused the EC to exceed 400 mS m<sup>-1</sup> was 384 Mg ha<sup>-1</sup> for all soils at Day 0 and Day 252, except for the Bo at Day 252. In this case the maximum EW application rate resulted in an EC over 400 mS m<sup>-1</sup>.

**Table 7.7** The electro-winning waste application rates at which the EC of the six soils were  $< 200 \text{ mS m}^{-1}$  and  $> 400 \text{ mS m}^{-1}$  for Day 0 and Day 252. The rate used in the laboratory investigations are given in parentheses ( $\text{g kg}^{-1}$ )

Sample day	Selection Criteria			
	EC $< 200 \text{ mS m}^{-1}$		EC $> 400 \text{ mS m}^{-1}$	
	0	252	0	252
Soil	Application rate ( $\text{Mg ha}^{-1}$ )			
Bonheim	48 (20)	48 (20)	384 (160)	768 (320)
Hutton	96 (40)	96 (40)	384 (160)	384 (160)
Inanda	96 (40)	96 (40)	384 (160)	384 (160)
Longlands	96 (40)	96 (40)	384 (160)	384 (160)
Shortlands	96 (40)	48 (20)	384 (160)	384 (160)
Valsrivier	48 (20)	96 (40)	384 (160)	384 (160)

## 7.4 Conclusions

These data suggest that the SS has a high liming ability, and that this can be maintained for a considerable period of time. Unfortunately, at the high application rates of SS, the pH becomes alkaline (typically  $> \text{pH } 7.5$ ) and this may cause nutrient deficiencies or, in organic soils, result in the solubilisation of organic material, potentially enhancing the mobilisation of metals in organo-metallic complexes. The rate at which this occurred varied for the different soil types, but appeared to be related to the initial pH of the soil. IN the more acidic soils higher rates could be applied than in the near-neutral soils. Under field conditions, increased leaching may increase the loss of basic cations released from the dissolving slag, and the neutralising effect of the SS will be less dramatic than was observed from the incubation experiment.

The EW tended to drive the soils to favourable pH conditions, especially at high application rates. However, the waste also introduces large amounts of soluble salts resulting in extreme soil salinity. Furthermore, there was also a tendency for the soils to acidify over time due to nitrification processes and liming may be required to prevent excessive generation of soil acidity in the longer term. The effect of the EW on the EC of the soils suggests that the disposal of the waste be limited to the two lowest rates tested here ( $20$  and  $40 \text{ g kg}^{-1}$ ), until the effects on plants, soil fauna and leachate properties can be investigated further, both under glasshouse conditions and in the field.

## CHAPTER 8

### EFFECT OF MANGANESE-RICH PROCESSING WASTES ON SOLUBLE AND EXTRACTABLE ELEMENTS OF SIX SOILS

#### 8.1 Introduction

It has been shown that both the SS and EW can influence the pH and salinity of different soils (Chapter 7). It is also important to assess the potential for the release of certain elements from the waste when applied to the soil. If excessively high amounts of an element are introduced into a soil system, the soil's assimilative capacity may be exceeded, and there exists the risk that these elements will migrate to groundwater and/or lead to toxicities in plants grown in the soil.

As highlighted in Section 5.2, some of the key processes involved in the interaction between waste and soil are sorption of cations and oxy-anions by Fe and Mn oxides, reactions with soil OM and precipitation of cations with anionic compounds. The capacity of a soil to render elements and compounds unavailable or immobile depends on the specific properties of the soil, including pH, CEC, mineralogy, organic matter and texture (Overcash and Pal, 1979). The behaviour of various cationic and anionic species, in relation to these soil parameters, are discussed in a number of introductory texts (Adriano, 1986; Fergusson, 1990; McBride, 1994; Kabata-Pendias, 2001; Sparks, 2003; Essington, 2004). This study investigated the changes in the amounts of selected elements from the SS or EW when applied to six soils of varying characteristics.

#### 8.2 Materials and methods

The same soils from the incubation experiment described in Chapter 7 were used in this study.

##### 8.2.1 Soluble elements

To assess changes in the concentrations of some key water-soluble elements, samples from Day 0 and Day 84 were extracted with distilled water (1:5 soil:water ratio) and the

concentrations of Ca, Fe, Mg, Mn and S measured by ICP-OES, for both SS and EW treatments and all soils. In the control and EW-treated soils Co concentrations were also determined by ICP-OES.

### 8.2.2 Extractable elements

The fractionation procedure described in Section 6.2.4 was also used to assess changes in the partitioning of selected metals in the waste-treated soils. Samples from Day 0, 3, 7, 14, 56, 84 and 140 were analysed. The exchangeable (EX, 0.05 M  $\text{CaCl}_2$ -extractable; Section 6.2.4) fraction was determined on all soils. The IB, OB and AMOX fractions (Section 6.2.4) were only determined for the Hu soil. The extracts were analysed for Co, Cu, Fe, Mn, Ni, Pb and Zn by AAS. The pH of the extracts was also measured.

## **8.3 Results and discussion**

### 8.3.1 Effect of slag

#### *8.3.1.1 Soluble elements*

Manganese concentrations of the SS-treated and control soils tended to be below detection, for both sampling times and in most of the soils, except the Ia (Table 8.1). In the Ia, at Day 0, there was an increase in soluble Mn with an increase in SS application rate. After 84 days the Mn concentrations for all treatments, in the Ia, had increased. However, by Day 84 both the 240 and 480  $\text{g kg}^{-1}$  SS treatments had lower Mn concentrations than the 120  $\text{g kg}^{-1}$  SS-treated soil. The concentration of soluble Fe varied markedly among the soils ranging from 5.87 to 356  $\text{mg kg}^{-1}$  for the control soils at Day 0 (Table 8.1). Generally, there was a decrease in the concentration of Fe at the higher SS application rates, while two of the soils (Bo and Va) had initial increases in Fe at the lowest SS application rate. At all SS application rates in the Bo, Hu, Sd and Va soils and at the higher SS application rates (60, 120, 240 and 480  $\text{g kg}^{-1}$ ) in the Lo soil, the concentrations of Fe decreased from Day 0 to Day 84. In the Ia the change over time was more variable, but considering the generally low Fe concentrations, the measured values may reflect sample variability.

**Table 8.1** Concentrations of water-soluble elements extracted from incubated Bonheim, Hutton, Inanda, Longlands, Shortlands and Valsrivier soils after the addition of slag from the Samancor Mn-smelter at rates of 0, 30, 60, 120, 240 and 480 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Soil	Application rate (g kg <sup>-1</sup> )	Sampling day											
		0		84		0		84		0		84	
		Mn		Fe		Ca		Mg		S			
Bonheim	0	bd	bd	356	162	20.1	17.3	40.8	19.5	5.8	14.2		
	30	bd	bd	407	77.4	33.4	33.3	48.8	27.9	110	90.9		
	60	bd	bd	315	14.8	28.9	84.7	42.0	51.5	42.5	94.1		
	120	bd	bd	301	3.78	40.9	110	48.5	72.3	45.3	122		
	240	0.91	bd	192	0.44	66.2	152	55.2	91.3	78.2	169		
	480	1.57	bd	24.6	bd	86.3	218	50.3	112	113	331		
Hutton	0	bd	bd	92.4	4.78	6.91	67.0	15.8	40.4	bd	15.2		
	30	bd	bd	83.7	0.17	16.1	156	19.2	74.6	39.0	147		
	60	bd	bd	88.9	bd	19.3	208	20.8	86.4	bd	151		
	120	bd	bd	72.2	bd	32.4	300	26.1	102	bd	176		
	240	bd	bd	64.6	bd	68.3	324	37.0	128	15.5	218		
	480	0.51	bd	19.3	bd	129	356	48.9	112	52.6	292		
Inanda	0	bd	2.23	5.87	bd	bd	36.7	1.90	14.0	17.8	19.8		
	30	1.56	7.03	6.71	0.75	5.04	112	3.81	64.4	39.3	109		
	60	2.72	61.5	7.51	3.02	9.41	178	5.65	105	19.6	181		
	120	21.1	103	5.71	6.86	45.1	336	16.1	169	60.9	284		
	240	31.6	86.1	8.02	1.83	92.8	370	27.2	160	102	310		
	480	41.1	67.1	4.93	5.26	217	355	50.6	131	194	345		
Longlands	0	bd	bd	91.5	113	bd	12.5	3.98	10.1	bd	6.12		
	30	bd	bd	79.7	85.9	8.39	52.9	7.61	20.9	64.3	42.0		
	60	bd	bd	61.2	56.3	29.5	82.6	12.7	24.5	44.0	63.1		
	120	0.30	bd	46.7	31.3	57.9	101	17.0	26.8	38.0	77.5		
	240	1.41	bd	34.9	5.27	89.8	141	22.0	35.4	61.5	133		
	480	bd	bd	5.80	bd	129	214	23.4	42.1	109	210		
Shortlands	0	bd	bd	152	124	bd	bd	10.3	12.6	bd	1.32		
	30	bd	1.77	155	96.7	2.40	82.9	15.2	51.9	13.8	63.8		
	60	bd	bd	85.1	6.24	16.0	150	22.2	78.9	bd	82.3		
	120	bd	bd	71.7	6.17	40.0	157	33.8	90.4	bd	93.9		
	240	bd	bd	37.0	3.26	89.6	168	50.5	112	38.1	134		
	480	bd	bd	13.2	0.21	124	219	54.7	104	75.6	214		
Valsrivier	0	bd	bd	177	482	5.13	23.5	48.0	130	bd	24.8		
	30	bd	bd	229	73.9	53.9	52.9	60.8	39.1	bd	54.7		
	60	bd	bd	179	13.7	29.3	68.3	56.3	29.8	bd	65.5		
	120	bd	bd	111	bd	48.8	112	51.3	38.9	bd	160		
	240	bd	bd	42.2	bd	53.7	149	41.4	46.8	4.6	191		
	480	bd	bd	bd	bd	110	231	43.2	48.5	64.9	280		

bd below detection

The Ca concentrations of all the soils tended to increase with increasing rates of SS applied. There was also an increase in Ca concentrations from Day 0 to Day 84 for the SS-

treated soils. The Mg and S concentrations of the soils also tended to increase with increasing application rates of SS, and also over time, following a similar pattern to that of Ca. It is clear that in the more acidic soils (notably the Ia) there was a greater release of certain metal ions, in particular, Mn. In the case of the water-soluble Mn (Table 8.1) this occurred almost exclusively in the Ia. Under natural weathering conditions (as in soil) the dissolution rate of silicates (olivines) is controlled by rates of surface reactions (Drever and Stillings, 1997, Jonckbloedt, 1998). The rate of dissolution depends on particle size, pH and temperature (Jonckbloedt, 1998), diffusion of reacting or product species through residual, micro-porous, leached layers and the presence of coatings formed on mineral surfaces (Gerard *et al.*, 2003). Considering that the Mn was mainly held in the mineral structure of the predominant minerals in the SS (Chapter 6), the higher acidity would have resulted in the dissolution of the minerals, releasing Mn, along with Ca, Mg and the other constituents. As expected, Ca and Mg concentrations in the Ia also increased, both with increasing SS application rates and time. However, it could be argued that higher Mn concentrations should have been measured for the other soils, as all the soils had elevated Ca concentrations due to the application of SS. Under oxidising and alkaline conditions, Mn precipitates as insoluble oxides, hydroxides and carbonates (McBride, 1994; Kabata-Pendias, 2001). Thus it is suggested that the higher pH of some of the SS-treated soils was the cause of the reduction in Mn concentrations. As was shown in Chapter 7, the SS-treated soils had pH values that were near-neutral or higher, with the exception of the Ia soil that tended to be acidic. The reduction in Fe concentrations of the SS-treated soils was also attributed to the increase in pH of the soils due to the addition of SS (Kabata-Pendias, 2001). The increases in S concentrations over time of the SS-treated soils were attributed to the release of S from oxidised minerals (perhaps barite, Section 6.3.6). In the control soils, the increase in S concentrations over time was probably due to the decomposition of organic material, releasing small amounts of S into solution

### 8.3.1.2 *Fractionation*

#### 8.3.1.2.1 *Exchangeable fraction*

Considerably higher concentrations of Mn were extracted from the SS-treated soils by the 0.05 M CaCl<sub>2</sub> than by distilled water, suggesting that most of the Mn was in an exchangeable form (Appendix 8.1). Generally, at Day 0, the addition of low rates of SS



resulted in an increase in Mn concentrations, but at the highest SS application rate (480 g kg<sup>-1</sup>) a decrease was noted relative to the 120 and 240 g kg<sup>-1</sup> treatments. The highest Mn concentrations were measured in the SS-treated Ia soil, even though the Ia control soil had the lowest Mn concentration. Overall, there was a decrease in Mn concentration over time for each soil type, though the time when this became evident varied between the soils. Generally, there was little change from Day 0 to Day 3, with a reduction in Mn concentrations noted only at the higher SS application rates (with the exception of the Ia soil). At Day 14 sharp decreases were observed in Mn concentrations of some treatments, in some soils notably the Bonheim, Hutton, Shortlands and Valsrivier soils. Exchangeable Mn concentrations of the SS-treated Ia and Longlands soils were relatively unchanged from earlier sampling times, except for the high EX-Mn concentration of the 480 g kg<sup>-1</sup> SS-treated Ia soil. From Day 28 the EX-Mn concentrations of most soils decreased, some soils to negligible values. In the Ia soil, the EX-Mn concentrations remained high at the four highest SS application rates, only decreasing at Day 140. Concentrations of the other metals tended to be low and no distinct patterns were evident that could be related to the application of SS. The Fe concentrations were considerably lower than measured in the water extractions. While no clear reason can be given it is speculated that the high pH of the CaCl<sub>2</sub> solution (> 8) caused the precipitation of Fe compounds, thereby reducing its availability.

The data from the EX-metal extractions indicated that higher concentrations of Mn were released in the more acidic soils, and that, typically, metal concentrations decreased over time as the pH of the soils increased due to the dissolution of the SS. It was noted that while the pure SS had very low concentrations of EX-Mn (Table 6.6) most of the SS-treated soils (except the Va) had higher concentrations of Mn than was the expected contribution from the added SS (Appendix 8.1), even after considering the contribution from the soil itself. This suggests that even low amounts of acidity may lead to the release of Mn from the SS applied to the soil, though in most instances Mn concentrations were relatively low compared to the control soils, except in the Ia.

#### **8.3.1.2.2      *Inorganically bound***

There were considerably higher amounts of IB-Mn than measured in the EX fraction, in the SS-treated Hu soil (Appendix 8.3). There was also not a marked change over time for

any of the treatments. The IB-Fe concentrations tended to increase with increasing rates of SS application. It appeared that at the lower SS application rates (30, 60 and 120 g kg<sup>-1</sup>) there was a reduction in Fe concentrations from Day 0 to Day 3, with Fe concentrations remaining below detection thereafter. The pattern was, however, not as clear at the higher SS application rates, where Fe concentrations tended to fluctuate dramatically between sampling days. Concentrations of the other metals were generally below detection, except for IB-Zn at, typically, the highest SS application rate and IB-Pb, at the two highest SS application rates. Again the changes over time did not show any distinctive trend.

#### **8.3.1.2.3      *Organically bound***

The amounts of OB-Mn in the SS-treated Hu were lower than the IB concentrations and did not vary greatly over time (Appendix 8.3). Concentrations of OB-Fe generally decreased with increasing SS application rates. The changes over time were not clear, though at the highest SS application rates there was a reduction in Fe concentration from about Day 28 to Day 140. Concentrations of OB-Co and OB-Zn also decreased with increasing rates of SS and over time. Concentrations of the other metals were more variable, with no distinct pattern evident.

#### **8.3.1.2.4      *Amorphous oxide bound***

Concentrations of AMOX-Mn, in the SS-treated soils, were high, though not as high as the IB fraction and there was little change over time (Appendix 8.3). The AMOX-Fe concentrations increased with increasing rates of SS application and decreased over time, notable after about Day 28. Concentrations of other AMOX metals were below detection, except for moderately high concentrations of Co in the control soils.

Overall, only the elevated Mn concentrations of the SS-treated soils for the IB, OB and AMOX fractions were directly attributable to the addition of SS to the soils (and to a lesser extent, IB-Fe). Generally, the OB and AMOX fractions are not a direct environmental risk as the conditions that these extractants mimic only occur in severely adverse environments. However, the elevated IB-Mn concentrations present some concerns for Mn toxicity and dispersal into the surrounding environment. Ross (1994) indicates that soil solution concentrations of Mn between 0.1 and 10 mg L<sup>-1</sup> can be considered as toxic. El-Jaoul and

Cox (1998) indicate that many crops are sensitive to soluble Mn in the soil at concentrations as low as  $1 \text{ mg kg}^{-1}$  and report critical limits of soluble Mn concentrations that cause injury to tobacco, peas and soybean of 1, 3.5 and  $10 \text{ mg kg}^{-1}$ , respectively. This suggests that under no circumstances should high rates of SS be applied to acidic soils. This may be a rather overly cautious suggestion in the light of some mitigating factors. It should be remembered that the extraction was conducted in a shaken 'test-tube' where the soil:solution ratio was not representative of the likely soil environment in which the waste may be disposed. The procedure used in the laboratory is likely to greatly exaggerate the potential negative effects of dissolution of the mineral components of the SS applied to the soil. Furthermore, the strong alkalising potential of the SS would further reduce the likelihood of such high amounts of metal being released from the waste. However, the alkalising effect of the slag may not be high enough, at the low rates of SS application, to increase the pH sufficiently to reduce the dissolution of the slag in an acidic soil.

### 8.3.2 Effect of electro-winning waste

#### *8.3.2.1 Soluble elements*

The concentrations of soluble Mn in the EW-treated soils increased sharply with an increase in application rate at Day 0 (Table 8.2). The same was evident at Day 84. There was also a general increase in Mn concentrations from Day 0 to Day 84 for most EW treatments (Table 8.2), probably due to increased acidity in the soils (Chapter 7). The Ia soil typically had the highest soluble Mn concentrations. At Day 0, Co concentrations increased with increasing application rates of EW (Table 8.2). The EW application rate at which Co was found in measurable amounts varied for the different soils, with the more acidic soils (Hu, Ia, Lo and Sd) tending to have higher Co concentrations, at the low EW application rates, than the less acidic Bo and Va soils. There was a decrease in Co concentrations over time for the Bo, Hu, Ia and Sd soils, while in the Va and Lo soils the concentrations remained similar from Day 0 to Day 84. There was a substantial decrease in soluble concentrations of Fe when EW was added to the soils, regardless of rate of application (Table 8.2). The concentrations of soluble Ca, in all soils, increased with an increase in EW application rate (Table 8.2). Typically the Ca concentrations of the 160 and  $320 \text{ g kg}^{-1}$  treatment were similar, perhaps suggesting that Ca concentrations at the high EW application rates were limited by the solubility of gypsum (Section 6.3.6).

**Table 8.2** Concentrations of water-soluble elements extracted from incubated Bonheim, Hutton, Ia, Longlands, Shortlands and Valsrivier soils after the addition of electro-winning waste from MMC at rates of 0, 20, 40, 80, 160 and 320 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Soil	Application rate (g kg <sup>-1</sup> )	Sampling day											
		0	84	0	84	0	84	0	84	0	84	0	84
		Mn		Co		Fe		Ca		Mg		S	
Bonheim	0	bd	bd	bd	bd	356	162	20.1	17.3	40.8	19.5	5.83	14.2
	20	23.2	51.0	bd	bd	bd	bd	335	473	231.7	284	948	867
	40	151	240	bd	bd	bd	bd	741	872	476	470	1919	1666
	80	486	689	0.97	1.39	bd	bd	1445	1430	762	689	3571	2755
	160	1322	972	6.14	1.46	bd	0.38	1969	1625	1020	768	6161	5111
	320	1799	2317	13.5	12.6	0.26	0.86	1723	1567	992	1036	9046	7910
Hutton	0	bd	bd	bd	bd	92.4	4.78	6.91	67.0	15.8	40.4	bd	15.2
	20	113	89.4	bd	bd	bd	bd	419	614	189	239	721	755
	40	352	277	1.38	bd	bd	bd	789	897	283	308	1487	1644
	80	812	579	4.22	bd	bd	bd	1217	1478	398	426	2847	3584
	160	1519	1625	7.98	5.03	bd	bd	1625	1715	519	563	4514	5754
	320	2273	2983	20.1	19.7	0.88	0.37	1600	1685	857	947	7089	9273
Inanda	0	bd	2.23	bd	bd	5.87	bd	bd	36.7	1.90	14.0	17.8	19.8
	20	287	309	0.05	bd	bd	bd	232	267	50.0	56.0	601	540.5
	40	597	559	1.32	0.75	0.04	0.07	462	487	87.3	84.1	1122	1261
	80	1170	1138	4.50	2.93	0.27	0.69	914	944	175	155	2271	2742
	160	2088	2089	15.4	9.42	0.85	0.92	1628	1528	478	340	5473	5917
	320	2908	3044	30.2	19.5	1.38	2.14	1744	1611	877	623	8341	8893
Longlands	0	bd	bd	0.45	bd	91.5	113	bd	12.5	3.98	10.1	bd	6.12
	20	113	141	0.79	bd	bd	0.13	347	453	61.9	78.4	547	795
	40	495	496	3.47	2.06	0.22	bd	906	759	151	133	1260	1686
	80	706	908	4.44	5.20	bd	bd	1279	1211	167	190	2262	3101
	160	1433	1632	10.4	9.37	0.39	bd	1773	1555	303	314	3910	5263
	320	1786	2463	15.4	18.0	0.81	bd	1700	1524	407	499	5216	7383
Shortlands	0	bd	bd	bd	bd	152	124	bd	bd	10.3	12.6	bd	1.32
	20	79.6	21.5	bd	bd	bd	bd	433	566	229	267	823	834
	40	192	78.4	0.15	bd	bd	bd	746	945	315	386	1430	1508
	80	460	220	1.58	bd	bd	bd	1168	1573	436	526	2334	3057
	160	1101	882	5.12	bd	bd	bd	1672	1740	582	639	4149	4552
	320	1827	2512	14.2	7.43	0.60	0.22	1647	1785	817	947	6356	7424
Valsrivier	0	bd	bd	bd	bd	177	482	5.13	23.5	48.0	130	bd	24.8
	20	61.5	62.3	bd	bd	bd	1.49	405	607	188	250	729	990
	40	315	202	0.40	bd	bd	bd	825	963	347	362	1800	1996
	80	774	867	3.25	2.82	bd	bd	1501	1459	489	492	2672	4051
	160	1470	1604	10.3	7.96	0.39	bd	1706	1595	677	65	5184	6195
	320	2516	2897	25.0	25.5	1.12	0.24	1744	1615	958	1084	7061	10471

bd below detection.

There was little change over time in the Ca concentrations of the soils. Soluble Mg concentrations also increased with an increase in EW application rate, but did not show a marked change over time. As was expected, S concentrations increased dramatically as application rates of EW increased, regardless of soil type. The S concentrations also tended

to increase over time (Table 8.2), indicating the dissolution of initially insoluble S-compounds (perhaps barite; Section 6.3.6).

The effect of EW on the soluble concentrations of certain elements was marked. Regardless of soil type, concentrations of Mn, Ca, Mg and S increased as EW application rates increased. The concentrations of these elements also increased over time suggesting increased solubilisation. As was the case for the SS-treated soils, the highest amounts of soluble elements were generally found in the Ia and Hu soils, attributed to their higher exchangeable acidity. Surprisingly, the Va soil also had elevated amounts of soluble elements. It is possible that the increase in exchangeable acidity and lowering of soil pH (Chapter 7), caused by the addition of EW, along with the low assimilative capacity of the Va may have led to the elevated concentrations of soluble elements.

### 8.3.2.2 *Fractionation*

#### 8.3.2.2.1 *Exchangeable fraction*

Manganese concentrations of the soils increased sharply when treated with EW (Appendix 8.2). Generally, Mn concentrations tended to increase over time for each respective treatment. Cobalt concentrations also increased with increasing EW application rates, though the change over time did not show any distinct trends (Appendix 8.2). As was the case for the SS, the concentrations of other metals tended to be low and not clearly related to EW application rates.

The EX-Mn concentrations were of particular concern. It was noted in Chapter 6 that the EW has a large amount of soluble Mn. It was expected that, in the soil environment, the Mn would be immobilised due to increased chemisorption and precipitation of insoluble Mn-compounds. These data clearly indicate that the Mn remains in a highly mobile phase. This, of course, implies the potential for severe environmental contamination (Section 8.3.2.1.4), especially if the EW is applied at the higher rates investigated here.

It appeared that the Lo soil immobilised the highest amounts of Mn, while the other soils promoted increased availability. As the Lo was selected as an unreactive soil, with negligible OC and CEC, it was anticipated that Mn concentrations might have been higher

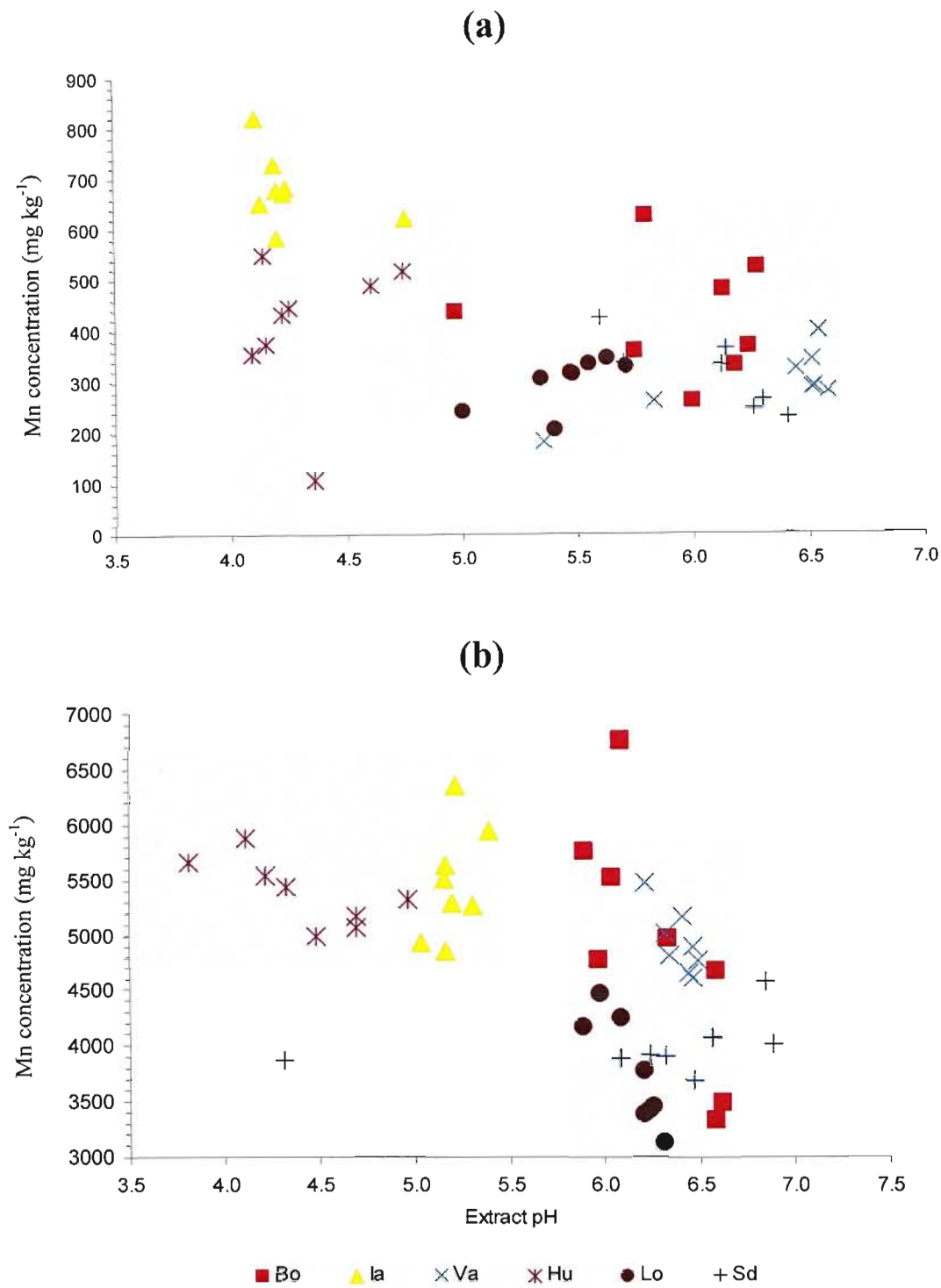
than some of the more reactive soils (e.g. Bo). This was intended to represent a worst-case scenario where maximum amounts of the Mn would be released from the EW applied to the soil. The initial impression was that the Lo soil sorbed or fixed the free Mn from the waste. As the Lo soil was coarse textured with a low CEC (Table 7.2), it was speculated that Mn coatings were forming on the surfaces of the sand grains. Various authors have reported on the formation of Mn coatings on sand or silica (Junta and Hochella, 1994; Junta-Rosso *et al.*, 1997; Hu *et al.*, 2004). Junta and Hochella (1994) argued that Mn (notably Mn (II)) in solution may adsorb and oxidise at various sites on a mineral surface, the most likely being broken edges, etches and cleavage lines on the surfaces of silica minerals. This would promote further Mn oxidation at these sites and 'islands' of Mn precipitates may form, removing Mn from solution. However, data presented in Section 6.3.5 showed that a) the waste contained about  $10\,437\text{ mg kg}^{-1}$  EX-Mn; and b) regardless of the waste:solution ratio approximately the same amount of Mn was extracted (Appendix 6.2). Thus the expected contribution of Mn from the EW was about 209 to  $3\,340\text{ mg kg}^{-1}$  for EW application rates of 20 to  $320\text{ g kg}^{-1}$ , respectively. The EX-Mn concentrations reported for the Lo soil (at Day 0) showed that the concentrations were similar to the expected contribution from the added EW (Appendix 8.2). This implies that in the Lo soil at Day 0, there was no marked interaction between the EW and the soil. This suggested that in the other soils, there was an immediate reaction between the EW and the soils to promote the release of greater amounts of Mn from the EW applied to the soils, this being particularly evident at the higher rates of application. For instance, at an EW application rate of  $320\text{ g kg}^{-1}$  at Day 0, all the soils (except for the Lo) had EX-Mn concentrations  $> 4\,000\text{ mg kg}^{-1}$ , which was higher than the expected contribution from the EW. Two possible mechanisms were considered to be the cause of this. Firstly, low pH may have caused the dissolution of oxide-bound Mn, leading to higher measured amounts of EX-Mn. Secondly, organic acids may have promoted dissolution of insoluble Mn-compounds and formed soluble organo-metallic complexes that were extractable with  $0.05\text{ M CaCl}_2$ . The equilibrium pH of the extracting solutions for the Lo soil, at the high EW application rates, were not markedly different than some of the other soils (e.g. Bo, Sd and Va; Appendix 8.2). The Lo also had a negligible OC content (Table 7.2). This suggested that reaction of the organic matter in the soils with the EW may be a key mechanism for the release of Mn from the waste.

There appeared to be some influence of pH on Mn dissolution in the EW-treated soils, though the strength of this influence did not seem to be marked. For instance, plots of EX-Mn concentrations against the equilibrium pH of the extracts, for the 20 and 320 g kg<sup>-1</sup> EW application rates across all soils, for all days, indicated that there were weak negative relationships in both cases (Figure 8.1). It is clear, however, that there was also a strong influence of soil type. Regardless of the EW application rate, there were groupings based on soil type. This suggests that, in addition to pH, other mechanisms for Mn release from the waste were involved, such as the effect of OC (and possibly mineralogy). The effect of OC is investigated in more detail in Section 8.4.

#### 8.3.2.2.2 *Inorganically bound*

The IB-Mn concentrations in the EW-treated Hu soil were higher than measured in the EX fraction (Appendix 8.4). This was not evident in the control soils. As expected, Mn concentrations increased with increasing rates of EW. At the lowest EW application rate (20 g kg<sup>-1</sup>) Mn concentrations, generally, increased from Day 0 to Day 28 and decreased thereafter to Day 140. At the other EW application rates the values tended to remain relatively constant at all sampling days.

The IB-Fe concentrations were generally below detection in the control soils and low EW treatments (20, 40 and 80 g kg<sup>-1</sup>). The IB-Fe concentrations increased sharply for the two highest EW application rates compared to the lower application rates, at all sampling times (Appendix 8.4). For the 160 g kg<sup>-1</sup> EW treatment there was a decrease in IB-Fe concentrations from about Day 56. At an EW application rate of 320 g kg<sup>-1</sup> the Fe concentrations tended to fluctuate over time and no clear pattern could be found. The concentrations of IB-Zn and IB-Co increased with increasing rates of EW. There were no apparent changes over time in the concentrations of IB-Zn and slight decreases in the concentrations of IB-Co from about Day 56 for all EW treatments.



**Figure 8.1** The relationship between final extract pH and 0.05 M CaCl<sub>2</sub>-extractable Mn concentrations, across all sampling days, for the different soils treated with (a) 20 and (b) 320 g kg<sup>-1</sup> of electro-winning waste.



The concentrations of IB-Cu, IB-Pb and IB-Ni also increased with increasing application rates of EW, though there were no distinct changes over time, except for the concentrations of IB-Pb at the highest EW application rate. In this instance, the IB-Pb concentrations increased from Day 0 to 14, then decreased again to Day 140.

#### **8.3.2.2.3      *Organically bound***

The concentrations of OB-Mn increased with increasing application rate of EW, though there appeared to be little change over time, except for the control and 20 g kg<sup>-1</sup> EW treatments that increased slightly from Day 0 to about Day 7 then remaining relatively constant (Appendix 8.4). The OB-Fe concentration increased slightly with addition of EW compared to the control, though the control soil also had relatively high OB-Fe concentrations. There were no marked changes over time. Concentrations of OB-Zn, OB-Co, OB-Cu, OB-Pb and OB-Ni tended to increase with increasing application rate of EW, though this was slightly variable for Zn, Cu and Ni (Appendix 8.4). Generally, there were no distinct changes over time for any these metals, except Pb that tended to increase over time especially at the lower EW application rates.

#### **8.3.2.2.4      *Amorphous oxide bound***

The concentrations of AMOX-Mn and AMOX-Fe increased with increasing application rate of EW, though, in the case of Fe, the control treatments also had high concentrations (Appendix 8.4). There did not appear to be any distinct changes over time for either of these metals. The concentrations of AMOX-Zn and AMOX-Ni were below detection at all EW application rates and sampling times. The concentrations of AMOX-Co and AMOX-Cu tended to increase with increasing rates of EW, though this was variable for Co concentrations (Appendix 8.4). The Co concentrations of the control soils were high, so the effect of adding the EW was not as marked as expected, considering the relatively high concentrations of Co in the EW (Chapter 6). There was no discernible change over time in the Co concentrations for any of the treatments. The AMOX-Cu concentrations were initially low (Day 0 to about Day 28) for the low EW application rates. However, from Day 56, the Cu concentrations of the low EW treatments increased. At the higher EW application rates Cu concentrations remained relatively static for all the sampling days.

Concentrations of AMOX-Pb were only measurable at the highest EW application rate, with concentrations remaining, largely, constant for all sampling times (Appendix 8.4).

## **8.4 Effect of organic acids on extractable Mn in soils treated with electro-winning waste**

### 8.4.1 Introduction

As the release of Mn from the EW was partly attributed to the presence of organic acids in some of the soils, it is pertinent to consider the basic chemistry of the interaction between Mn and organic acids, in particular humic substances (HS). Humic substances form the major component of soil organic carbon (Senesi and Loffredo, 2005) and consist of alkali-soluble humic acid (HA), acid-soluble fulvic acid (FA) and insoluble humin (Essington, 2004). Humic substances can interact with metal ions in the soil to form water-soluble, colloidal and water-insoluble complexes that may both increase or decrease metal availability in the soils, depending on the specific properties of the HS-metal complex and also the soil properties (Stevenson, 1982; Senesi and Loffredo, 2005). Humic and fulvic acids are complex molecules that possess many complexing sites, where the most common functional groups that bind metals are O-containing groups (e.g. carboxylic, phenolic, alcoholic), but also include certain amino groups and S- and P-containing groups (Essington, 2004; Senesi and Loffredo, 2005).

Inorganic cations are divided into three classes depending on their reactivity with organic ligands (Senesi and Loffredo, 2005). These are ‘hard’ cations (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) that are generally involved in weak electrostatic interactions; ‘soft’ cations (e.g.  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ) that tend to form strong covalent bonds with intermediate (N) and soft (S) ligands; and ‘borderline’ cations (e.g.  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) that possess appreciable affinity for both hard and soft ligands. Senesi and Loffredo (2005) indicated that ligands preferred by ‘borderline’ cations, such as Mn, include primary, secondary and tertiary amino groups and amides. In general, competition for a ligand involves ‘hard’ and ‘borderline’ cations for O-sites, and ‘soft’; and borderline” cations for N- and S-sites (Senesi and Loffredo, 2005). The affinity of soil OM for divalent metal cations tends to parallel metal electronegativity values, but is highly dependent on the properties of the OM and pH (Senesi and Loffredo, 2005). Kabata-Pendias (2001) indicate that the general order of the stability constants for

various metallo-organic complexes, again depending on pH and properties of the OM, follows the sequence:  $U > Hg > Sn > Pb > Cu > Ni > Co > Fe > Cd > Zn > Mn > Sr$ . Because of the variable nature of the OM and the effect of other soil properties this sequence may vary. For instance, the stability constants reported for metal affinities for HA at pH 3.7 are:  $Hg > Fe > Pb > Cr > Cu > Zn > Cd > Mn > Co$ , while the order of the affinity of metal ions to form water-insoluble complexes with FA follows the sequence:  $Fe = Cr = Al > Pb = Cu > Hg > Zn = Ni = Co = Cd = Mn$  (Kabata-Pendias, 2001).

Metal ions can affect the solubility of HA and FA in two different ways (Stevenson, 1982, Senesi and Loffredo, 2005). In brief, when HA and FA are dissolved in water, dissociation of the acidic functional groups occurs and results in a “stretched” configuration of the molecule due to repulsive charges. The addition of metal cations reduces these negative charges, due to salt formation and collapse of the organic molecule, decreasing solubility. Polyvalent metal ions may also coordinate with ligands that belong to two or more organic molecules, producing single chain-like structures that may aggregate and precipitate, especially at high metal to ligand ratios. Essington (2004) indicated that, for HA, an increase in salt concentrations or lowering of pH, collapse the random thread-like coils, that exist at low salt concentration and high pH, into ring-like structures that may precipitate. Generally, FA-metal complexes tend to be more soluble than HA-metal complexes because of the higher acidity and lower molecular weight of the FA (Stevenson, 1982). In the case of Mn, the partially filled *d*-orbitals in the electronic structure are conducive to the formation of complexes with low molecular weight organic acids and amino groups and is favoured with increasing pH as more functional groups on the organic component (i.e., HA and FA) become reactive (Hue, 1988).

The above discussion suggests that, typically, OM present in the soil will immobilise free metallic ions into largely unavailable forms. In addition, at high salt concentrations the metal-organo complexes may precipitate, reducing metal availability further. For the purposes of this study, it was speculated that soils with appreciable amounts of OM would, in part, assimilate the free Mn introduced to the soil when EW was applied. This is contradictory to the findings thus far. The presence of OM in the soils, even at low amounts, appears to promote the release of Mn from the EW and increase solubility and availability. Some authors, however, have reported on increased Mn solubility and

mobility in soils in the presence of applied OM (Cotter and Mishra, 1968; Mandal and Mitra, 1982; Hue, 1988; Vega *et al.*, 1992; Hue *et al.*, 2001; Hue and Mai, 2002).

The effect of incubating an alkaline, alluvial soil at field capacity with OM (weathered cotton seed hulls) added at rates of 0, 2, 4, 8 and 16% was investigated by Cotter and Mishra (1968). They found that there was an increase in exchangeable Mn concentrations (neutral ammonium acetate-extractable) with increasing rates of the OM. This effect was observed from Day 0 (fresh mixtures). There was also an increase in Mn concentrations over time for most of the treatments, though at extended incubation times (5 to 9 days), at low OM application rates (2 and 4%) Mn re-oxidised to an unavailable form. The increase in Mn concentrations was attributed to the creation of reducing conditions due to rapid oxidation of OM added to the soil. Mandal and Mitra (1982) reported that the addition of OM (as starch) to an alluvial, saline and acid soil resulted in an increase in the amounts of water-soluble and exchangeable Mn, but not in a lateritic soil. They did not propose a mechanism for the increase though.

Hue (1988) found that addition of sewage sludge (SeSl), at rates of 20, 40 and 80 g kg<sup>-1</sup>, to a manganiferous, Hawaiian Oxisol (15 000 mg total Mn kg<sup>-1</sup>) led to phytotoxic levels of Mn in lettuce, and SS applied at 80 g kg<sup>-1</sup> to a moderately manganiferous, alkaline Vertisol (2 300 mg total Mn kg<sup>-1</sup>) led to phytotoxicity in lettuce. The phytotoxicity was directly related to the soil-solution Mn concentrations, where in both soils, increases in SeSl application resulted in increases in Mn concentrations, irrespective of soil pH. Hue (1988) proposed that pH was not a determining factor in the release of Mn from the soils, but that a reducing environment, caused by rapid oxidation of the applied SeSl, and complexation with organic acids were the principal driving factors. Hue (1988) found elevated concentrations of several organic acids and suggested that these resulted in the dissolution of soil Mn and the formation of water-soluble organic-metal complexes. Vega *et al.* (1992) reported that cowpea showed Mn toxicity symptoms when grown on a manganiferous Oxisol treated with SeSl. They also found that soluble Mn concentrations increased after SeSl application to the soil, but only at pH 4.0 and 5.5. At higher pH values, Mn concentrations of both the soil solution and cowpea foliage decreased substantially.

Hue *et al.* (2001) investigated the dissolution of Mn from a manganiferous Oxisol by simple organic acids and the effect of OM additions on Mn-availability to soyabeans. They

found that organic molecules containing OH-OH groups in the ortho-position or S-H groups increased the dissolution of Mn from the Oxisol. They also reported that the addition of either cowpea green-manure or biosolids to the Oxisol aggravated Mn phytotoxicity in the soyabeans, relative to the control soils. This was attributed to dissolution and complexation of Mn from the soil by the organic manures. The effect of pH and the addition of two composts (made from chicken manure and SeSl) on Mn uptake by watermelon on a manganiferous Oxisol was investigated by Hue and Mai (2002). They found that addition of OM to the soil caused Mn toxicity in the watermelon, but that liming the soil to about pH 6.5 could mitigate the toxicity effect. They attributed the increased Mn concentrations in the OM-treated soil to the formation of organic acids that promoted Mn dissolution and complexation.

The findings from these investigations suggest that, in some circumstances, OM may promote the dissolution and availability of insoluble Mn-phases. To test if the presence of OC in the soils used in this study was, at least in part, responsible for the increased Mn concentrations over the expected amounts in the EW-treated soils, two additional studies were conducted. The first investigated the removal of OC from the soil and the second considered the effect of reintroducing organic acids to the soils.

#### 8.4.2 Materials and methods

##### *8.4.2.1 Removal of organic carbon*

The six soils used previously were treated with  $\text{H}_2\text{O}_2$  (Misra and Mishra, 1967) and gentle heating to remove reactive OC. The soils were then air-dried and milled to pass through a 2 mm sieve. Electro-winning waste was added to the soils at rates of 20 and 320 g  $\text{kg}^{-1}$  (the lowest and highest EW application rates tested previously). As the previous incubation experiment (Section 8.3.2) found that Mn was released at Day 0 the mixtures were not incubated, but extracted immediately. The EW-treated and control soils were extracted with 0.05 M  $\text{CaCl}_2$  (Section 6.2.4) and concentrations of Co and Mn in the extracts measured by AAS.

#### 8.4.2.2 *Addition of organic acids*

Organic acids (HA and FA) were added to the H<sub>2</sub>O<sub>2</sub> treated soils and EW-treated soils (as used above) to simulate the effect of organic acids in the soil. The HA and FA were commercially available agricultural grade products. The use of A.R. grade or purified organic acids was not considered necessary for the purposes of this investigation. The assay of the HA, as supplied, is given in Appendix 8.5, but an assay was not available for the FA. The HA was supplied as a dry, granular, product and the FA was supplied as a 5% solution (pH 5.3). The HA was added to the soils at rates of 0, 5, 10 and 20 g kg<sup>-1</sup> (0, 0.5, 1 and 2%) and the FA was added at a rate of 5 g kg<sup>-1</sup> (0.5%). Only a single rate of FA was tested due to limited quantities of the supplied FA. As before, the samples were extracted with 0.05 M CaCl<sub>2</sub>, immediately after mixing. The concentrations of Co and Mn in the extracts were measured by AAS and the pH of the extracts was also measured.

### 8.4.3 Results and discussion

#### 8.4.3.1 *Effect of removal of organic carbon*

Generally, there was an increase in the Mn concentrations after treatment with H<sub>2</sub>O<sub>2</sub> in the control soils, except for the Lo soil (Table 8.3). This increase was most marked for the Bo and Sd soils. The concentrations of Co also increased in the Bo and Sd control soils after treatment with H<sub>2</sub>O<sub>2</sub>. This was attributed to the release of these metals bound by organic matter which was oxidised by the H<sub>2</sub>O<sub>2</sub>. The Co concentrations remained relatively unchanged in the other soils.

If the Mn contributed by the soil is deducted from the amount measured when assessing the amount of Mn attributable to the addition of the EW then, in most cases, the Mn concentrations approximate the expected contribution from the EW. For example, in the Bo soil about 246 mg kg<sup>-1</sup> Mn was attributed to the addition of EW after correcting for the contribution of Mn from the H<sub>2</sub>O<sub>2</sub> treated soil. Generally, the corrected Mn values were slightly higher than the expected amount, except for the Va soil, where the Mn concentration was lower than expected. At the low application rate of EW (20 g kg<sup>-1</sup>), the concentrations of Mn increased, relative to the original extraction, in the Bo, Hu, Lo and Sd soils and decreased in the Ia and Va soils. In all cases, perhaps with the exception of the

Lo soil, Mn concentrations were still higher than the expected contribution from the EW (about 209 mg kg<sup>-1</sup>). However, it must be noted that most of the control soils showed a marked increase in Mn concentrations after treatment with H<sub>2</sub>O<sub>2</sub>.

Generally, at the higher EW application rate (320 g kg<sup>-1</sup>) Mn concentrations in soils treated with H<sub>2</sub>O<sub>2</sub> were lower than measured in the 'original' untreated soils. When the Mn concentrations were corrected for the expected contribution from the control soil, then most soils had Mn concentrations similar to the expected contribution from the EW (3 340 mg kg<sup>-1</sup>).

**Table 8.3** The effect of removing organic matter (treatment with H<sub>2</sub>O<sub>2</sub>) on the 0.05 M CaCl<sub>2</sub>-extractable Mn concentrations of six soils treated with electro-winning waste at rates of 0, 20 and 320 g kg<sup>-1</sup>. The results from the original extractions (from Appendix 8.2) are given for convenience

Soil	Application rate (g kg <sup>-1</sup> )	Mn		Co	
		Original	H <sub>2</sub> O <sub>2</sub>	Original	H <sub>2</sub> O <sub>2</sub>
		(mg kg <sup>-1</sup> )			
Bonheim	0	149	1196	1.30	11.3
	20	477	1419	1.10	13.3
	320	4662	4537	14.9	33.0
Hutton	0	120	325	1.80	1.90
	20	488	605	2.29	3.00
	320	4998	3705	25.6	23.8
Inanda	0	9.99	16.4	0.80	bd
	20	650	356	3.89	bd
	320	6355	4266	30.3	35.9
Longlands	0	31.9	bd	4.29	bd
	20	204	267	4.29	bd
	320	3130	3378	18.1	23.1
Shortlands	0	1224	932	3.20	22.5
	20	226	1210	2.70	41.9
	320	4059	3898	17.9	23.2
Valsrivier	0	25.5	159	bd	bd
	20	396	332	1.40	bd
	320	4645	3813	22.8	24.2

bd below detection.

For instance, in the Sd soil, the corrected Mn concentration<sup>2</sup> was about 3 265 mg kg<sup>-1</sup> and in the Hu soil it was about 3 484 mg kg<sup>-1</sup>. In the Ia soil the Mn concentration remained higher (about 4 261 mg kg<sup>-1</sup>) than the expected concentration. Comparing this value to the corrected Mn concentration of the original extraction (about 6 351 mg kg<sup>-1</sup>), a substantial reduction was evident. In the Lo soil the Mn concentration remained relatively unchanged from the original extraction, perhaps reflecting the initially very low OC content of this soil (Section 7.3.1).

The Co concentrations remained relatively unchanged in all soils except for the Bo. In this instance there was an increase for all treatments, thus the Co concentration of the EW treatments was probably due to the effect of the soil, rather than the EW (Table 8.3).

#### 8.4.3.2 *Effect of adding organic acids*

In most instances, there was an increase in Mn concentrations at the high EW application rate, after the addition of either HA or FA, relative to the soils only treated with H<sub>2</sub>O<sub>2</sub> (Table 8.4). These increases were not always evident at the low EW application rate. The contribution of Mn from the HA was considered negligible (Appendix 8.5).

In the Bo, at the 320 g kg<sup>-1</sup> EW treatment, EX-Mn concentrations increased when the HA application rate increased from 0.5 to 1%, while the Mn concentration of the 2% HA treatment was similar to that of the 1% HA and 0.5% FA treatment. In the control soil and 20 g kg<sup>-1</sup> EW treatment, Mn concentrations remained relatively constant regardless of the type or rate of organic acid used, while the concentrations of Mn in the 20 g kg<sup>-1</sup> EW treatment were similar to what was expected from the addition of the EW. This indicates that at the high EW application rate, these organic acids may have promoted the dissolution of Mn-rich minerals in the EW applied to the soil.

<sup>2</sup> The 'corrected Mn concentration' was calculated by considering the contribution of Mn from both the amount of EW added to the soil and the amount from the control soil, relative to the ratio of EW to soil. For example, in the H<sub>2</sub>O<sub>2</sub> treated Sd soil with 320 g kg<sup>-1</sup> EW, 3 898 mg kg<sup>-1</sup> EX-Mn was measured. The contribution of the control soil was 68% of 932 mg kg<sup>-1</sup> (= 634 mg kg<sup>-1</sup>). Therefore the contribution attributed to the EW was 3 898 - 634 = 3 265 mg kg<sup>-1</sup>  $\approx$  3 340 mg kg<sup>-1</sup> (the expected contribution).



**Table 8.4**      Effect of adding humic acid (at rates of 0.5, 1 and 2%) and fulvic acid (at a rate of 0.5%), to six soils (treated with H<sub>2</sub>O<sub>2</sub> to remove organic matter) with electro-winning waste (EW) applied at rates of 0, 20 and 320 g kg<sup>-1</sup> on concentrations of 0.05 M CaCl<sub>2</sub>-extractable Mn, Co and extract pH

Soil	Organic acid	EW application rate (g kg <sup>-1</sup> )	Application rate (%)	Final extract pH	Mn                      Co	
					----- (mg kg <sup>-1</sup> ) -----	
Bonheim	Humic	0	0.5	4.3	1191	18.9
		20		4.5	1444	20.9
		320		5.5	5291	49.4
		0	1	4.7	1239	18.4
		20		4.8	1501	20.3
		320		5.9	5526	49.8
		0	2	5.0	1108	15.8
		20		5.8	1379	17.5
		320		6.0	5481	43.9
	Fulvic	0	0.5	4.6	1164	18.0
		20		4.4	1489	21.4
		320		4.9	5519	49.2
Hutton	Humic	0	0.5	5.1	292	5.18
		20		5.1	569	7.74
		320		5.6	4874	38.8
		0	1	5.2	299	4.53
		20		5.3	584	6.67
		320		5.8	4517	33.5
		0	2	5.5	284	3.26
		20		5.6	433	3.56
		320		6.2	4263	27.7
	Fulvic	0	0.5	4.7	326	4.58
		20		4.7	589	6.32
		320		5.0	5391	46.3
Inanda	Humic	0	0.5	4.2	14.8	0.72
		20		4.3	241	2.94
		320		5.5	4566	37.8
		0	1	4.4	10.3	1.34
		20		4.4	340	3.86
		320		4.6	4633	43.4
		0	2	4.5	6.35	0.80
		20		4.5	408	4.13
		320		4.8	4674	38.8
	Fulvic	0	0.5	4.4	10.0	0.62
		20		4.4	305	3.71
		320		4.7	5297	44.0

**Table 8.4 (contd.).** Effect of adding humic acid (at rates of 0.5, 1 and 2%) and fulvic acid (at a rate of 0.5%), to six soils (treated with H<sub>2</sub>O<sub>2</sub> to remove organic matter) with electro-winning waste (EW) applied at rates of 0, 20 and 320 g kg<sup>-1</sup> on concentrations of 0.05 M CaCl<sub>2</sub>-extractable Mn, Co and extract pH.

Soil	Organic acid	EW application rate (g kg <sup>-1</sup> )	Application rate (%)	Final extract pH	Mn	Co
					----- (mg kg <sup>-1</sup> ) -----	
Longlands	Humic	0	0.5	6.3	bd	1.39
		20		6.7	299	2.99
		320		6.5	4150	28.8
		0	1	6.6	1.82	1.27
		20		6.9	191	2.14
		320		6.7	3608	22.4
		0	2	6.9	bd	0.30
		20		7.2	238	1.84
		320		6.9	2909	14.1
	Fulvic	0	0.5	4.7	23.7	1.00
		20		4.8	289	3.11
		320		5.2	4185	34.3
Shortlands	Humic	0	0.5	6.4	847	6.60
		20		6.1	1107	8.39
		320		6.3	5379	38.6
		0	1	6.3	858	5.75
		20		6.5	995	6.37
		320		6.3	4176	22.2
		0	2	6.9	769	4.16
		20		6.8	941	5.10
		320		6.5	4338	22.0
	Fulvic	0	0.5	4.8	999	9.38
		20		4.9	1203	12.0
		320		5.3	5517	45.6
Valsrivier	Humic	0	0.5	6.1	151	2.84
		20		6.4	365	4.55
		320		6.4	4653	37.4
		0	1	6.5	125	2.19
		20		6.6	374	3.33
		320		6.6	4270	26.4
		0	2	6.9	123	1.69
		20		6.9	248	2.46
		320		6.7	3909	19.1
	Fulvic	0	0.5	4.7	188	3.73
		20		4.7	422	5.50
		320		5.2	4445	37.8

bd below detection.

In the Ia soil, there was only a marginal increase in Mn concentrations, at the high EW application rate, of the HA treated soils (4 566, 4 633 and 4 674 mg kg<sup>-1</sup> for the 0.5, 1 and 2% HA treatments, respectively; Table 8.4), when compared to the H<sub>2</sub>O<sub>2</sub>-treated soil (4266 mg kg<sup>-1</sup>; Table 8.3). At the low EW application rate there were also small increases in Mn concentrations with increasing application rates of HA (241, 340 and 408 mg kg<sup>-1</sup> for the 0.5, 1 and 2% HA treatments, respectively; Table 8.4). The Mn concentration of the Ia soil treated with the high EW application rate and FA was greater than any of the HA treatments.

In the Lo soil there was a marked increase in Mn concentrations at only the lowest HA treatment (0.5%) and the FA treatment, at the highest EW application rate, when compared to the original extractions. At higher HA application rates (1 and 2%) the EX-Mn concentrations of the Lo soil decreased. This was attributed to an increase in the pH at the higher HA application rates due to the high pH of the HA (Appendix 8.5) and the low buffering capacity of the Lo soil.

A similar situation, to that of the Lo, existed for the Hu, Sd and Va soils, though Mn concentrations still remained higher in these soils than the expected contribution from either the EW or the soil, suggesting that the HA was acting to release Mn from the EW added to these soils. As with all the other soils, the Mn concentrations of the FA-treated soils tended to be higher than for the HA treatments, attributed to the lower pH of the FA compared to the HA.

Generally, Co concentrations decreased at both the high and low EW application rates as HA application rates increased, with the exception of the Ia and Bo soils. In these two soils the Co concentrations remained relatively constant regardless of the amount of HA added. The Co concentrations of the FA-treated soils were also typically higher than the HA or untreated soils, perhaps due to the lower pH of the FA compared to the HA.

## 8.5 Conclusions

These data suggest that both pH and the presence of OM in the soils was responsible for the higher than expected amounts of Mn in the EW-treated soils, especially at the high EW application rates. The influence of OM appeared to be greater than the influence of pH.

The original Va soil was an anomaly, as it had low amounts of OC and moderately high pH (Section 7.3.1). However, the data showed that after the soil was treated with  $H_2O_2$ , lower amounts of Mn were extracted, and that the introduction of organic acids increased extractable Mn concentrations in EW-treated soils. The OM present in the Va soil may be of a highly reactive nature, and even at low concentrations had a marked influence on Mn concentrations. The data also supported the conclusion that the Lo soil was unreactive, as removal of OM did not dramatically alter EX-Mn concentrations, while the addition of HA and FA (at low application rates) resulted in increased EX-Mn concentrations. The data for the other soils supported the hypothesis that OM led to increased dissolution of Mn in the EW when applied to the soil. While increases in Mn concentrations were partly attributed to the influence of pH the absolute effect was not determined. Furthermore, the forms or types of organic acids present in the different soils was not investigated and this may be of importance as suggested by the results obtained for the Va soil.

## **CHAPTER 9**

### **THE GROWTH OF RYEGRASS IN SOILS TREATED WITH SLAG OR ELECTRO-WINNING WASTE**

#### **9.1 Introduction**

An important aspect that must be considered when applying a waste to land is the likely effect that the waste may have on the performance and nutrient uptake by plants grown in soil treated with the waste. Up to this point, in this investigation, the potential risk that either the SS or EW posed to the environment was based on laboratory extractions that may not necessarily reflect what is occurring in a given volume of soil under field conditions. Pot experiments may offer some insight into this aspect of the land application of the waste, and give a more realistic reflection of the likely uptake of an element from the soil, by plants, than can be estimated from a value obtained from an extractant. While not without their drawbacks, pot experiments can assist in defining the parameters that may be cause for concern. These can then be considered when implementing field-scale studies that investigate the land application of a waste.

The objectives of the following investigations were thus:

- to assess the effect of applying either SS or EW to two different soils on the yield and nutrient uptake of ryegrass; and
- to investigate some ameliorative treatments to improve the growth of ryegrass grown in a Hu soil treated with low rates of EW.

#### **9.2 Materials and methods**

##### 9.2.1 Pot experiment 1

Two soils were selected for the preliminary pot experiment (Lo and Hu). Soil was placed in a 1.1 L plastic pot (with a fine glass-wool membrane placed over the drainage-holes), lightly tapped a few times and the mass of material determined (1.5 and 1.2 kg for the Lo and Hu soils, respectively). This gave bulk densities of approximately 1.5 and 1.2 g cm<sup>-3</sup> for the Lo and Hu soils, respectively. These masses were then used as the basis for all subsequent calculations, and all pots were filled with mixtures of soil (Lo or Hu) and < 2

mm waste (SS or EW) to the respective masses of the untreated soils. The SS was mixed with the soils at rates of 30, 60, 120, 240 and 480 g kg<sup>-1</sup> and the EW at 20, 40, 80, 160 and 320 g kg<sup>-1</sup>, as well as unamended treatments of soil (control pots), as used in the incubation investigation.

Perennial ryegrass (*Lolium perenne*) was used as a test crop. About 20 seeds were planted in each pot. Pots were watered as necessary to ensure the soil remained moist, but not waterlogged. Four weeks after germination, the seedlings were thinned to four plants per pot. The pots were not fertilised.

Pots were arranged in three blocks (replicates) according to the random design generated by the statistical package Genstat 8.1. Each pot was placed on a collecting tray, to prevent loss of sediment and water. The mean glasshouse temperature range was from 14 to 28 °C (min = 11 °C, max = 37 °C) for the duration of the trial.

The plants were harvested after 10 weeks (H1), and again after a further 8 weeks growth (H2), by cutting the plants about 10 mm above the soil surface. The harvested material was placed in paper bags and dried at 65 °C for 2 days in a forced draft oven. After drying, plant biomass was determined and the material milled. The total yield was determined for the experiment by summation of the yield from H1 and H2. In some instances, due to poor growth, there was inadequate plant material for chemical analysis, so the replicates for each treatment were bulked and used for analysis. This was not possible for the yield of ryegrass grown in the Lo soil treated with SS at an application rate of 480 g kg<sup>-1</sup> due to the low yield at H1.

Plant material was digested in nitric acid (Appendix 4.5) and concentrations of Cu, Co, Fe, Mn, Pb, Ni, Zn, Na, Ca, Mg, K, P and S determined by ICP. Total N was determined by Kjeldahl digest (Bremner and Mulvaney, 1982).

Growth of the ryegrass in the EW-treated soils was generally very poor, so statistical analyses were not possible. The effect of soil type and SS application rate on the total yield of ryegrass was compared by two-way ANOVA (Genstat 8.1). Where the overall difference was found to be significant the means were compared by LSD at the 5% level of significance. The best correlation between the yield of ryegrass and SS application rate for

each soil type were determined using the regression and curve fitting functions available in Microsoft Excel, using the coefficient of determination ( $R^2$ ) as the criteria for best fit. Due to lack of replicates in the SS-treated Lo soil, due to bulking of plant material for chemical analysis, statistical analysis was not conducted.

### 9.2.2 Pot experiment 2

A second pot experiment using only the Hu soil and EW was conducted to investigate some treatments to ameliorate the high levels of readily extractable Mn found in the EW. The first pot experiment showed that ryegrass could not be grown in EW-treated Hu soil at rates greater than  $40 \text{ g kg}^{-1}$ , thus this was set as the upper limit for application in this investigation. In addition, data from Section 8.5.3.2 suggested that, at low application rates of EW, the addition of  $20 \text{ g kg}^{-1}$  HA may slightly reduce available Mn concentrations in soil-applied EW. To test this,  $1.2 \text{ kg}$  of Hu soil treated with EW at rates of 0, 10, 20 and  $40 \text{ g kg}^{-1}$  were mixed with either HA (Appendix 8.5) or a commercially available compost (Gromor, air-dried and sieved to  $< 1 \text{ mm}$ ) at rates of either 0 or  $20 \text{ g kg}^{-1}$  (Table 9.1). To determine if increasing the soil pH (adding lime) would improve the remedial action of the organic matter, lime (laboratory grade  $\text{CaCO}_3$ ) was added at rates equivalent to 0, 5 and  $10 \text{ Mg ha}^{-1}$  to the treatments containing organic matter.

The preliminary pot experiment suggested that P deficiency was likely in the EW-treated soils. The fertility analysis supplied by the Soil Fertility and Analytical Services Division (KwaZulu-Natal Department of Agriculture, Cedara) recommended that about  $65 \text{ kg P ha}^{-1}$  be added to the Hu soil. This was added as  $\text{NH}_4\text{H}_2\text{PO}_4$ . This fertiliser was selected as the control Hu soil was deficient in N and the addition of  $\text{NH}_4^+$  to the EW treatments was not considered to be a problem given the existing high concentrations in the waste.

Pots were arranged in three blocks (replicates) in a randomised design. About 20 seeds of perennial ryegrass were planted in each pot. Pots were watered to ensure the soil remained moist, but not waterlogged. Four weeks after germination the seedlings were thinned to six plants per pot. The plants were harvested after 8 weeks of growth (H1) and again after a further 6 weeks (H2) by cutting the plants about 10 mm above the soil surface. The harvested material was placed in paper bags and dried at  $65^\circ\text{C}$  for 2 days in a forced draft

oven. After drying, plant biomass was determined, and the material milled. Ryegrass yields were compared by ANOVA for H1 and H2 and for total yield.

Plant material was digested in nitric acid (Appendix 4.5) and Cu, Fe, Mn, Zn, Ca, Mg and K determined by AAS. Phosphorus concentrations were determined colorimetrically (The Non-Affiliated Soil Analysis Work Committee, 1990). Total N was determined by Kjeldahl digestion (Bremner and Mulvaney, 1982).

**Table 9.1** Treatments applied in the second pot experiment

<b>Treatment number</b>	<b>Electro-winning waste (g kg<sup>-1</sup>)</b>	<b>Treatment (Organic matter source + Lime (Mg ha<sup>-1</sup>))</b>
1	0	
2	10	20 g kg <sup>-1</sup> humic acid + 0 Mg ha <sup>-1</sup> lime
3	20	
4	40	
5	0	
6	10	20 g kg <sup>-1</sup> humic acid + 5 Mg ha <sup>-1</sup> lime
7	20	
8	40	
9	0	
10	10	20 g kg <sup>-1</sup> humic acid + 10 Mg ha <sup>-1</sup> lime
11	20	
12	40	
13	0	
14	10	20 g kg <sup>-1</sup> compost + 0 Mg ha <sup>-1</sup> lime
15	20	
16	40	
17	0	
18	10	20 g kg <sup>-1</sup> compost + 5 Mg ha <sup>-1</sup> lime
19	20	
20	40	
21	0	
22	10	20 g kg <sup>-1</sup> compost + 10 Mg ha <sup>-1</sup> lime
23	20	
24	40	
25	0	
26	10	Control (No organic matter or lime)
27	20	
28	40	



To assess the effect of the treatments (Table 9.1) on the  $\text{pH}_{\text{water}}$ , EC and 0.05 M  $\text{CaCl}_2$ -extractable Mn concentrations a ‘mini’ incubation experiment was designed. While soil from the pot experiment could have been used for this investigation, it was considered necessary to exclude the possible influence of root growth on soil characteristics, hence a separate incubation experiment was carried out. Sealable, plastic vials were filled with about 100 g of the soil and treatment mixtures described for the pot experiment (Table 9.1). These were wet to field capacity, thoroughly mixed and then incubated at 25 °C for 21 days. To prevent anaerobic conditions from developing in the vials, they were opened every second day and remixed. After the incubation period the samples were air-dried and milled to pass through a 2 mm sieve. The  $\text{pH}_{\text{water}}$  and EC of the samples were determined as described in Chapter 4, and Mn concentrations determined by extraction with 0.05 M  $\text{CaCl}_2$ , as described in Chapter 6.

### 9.2.3 Leaching column experiment

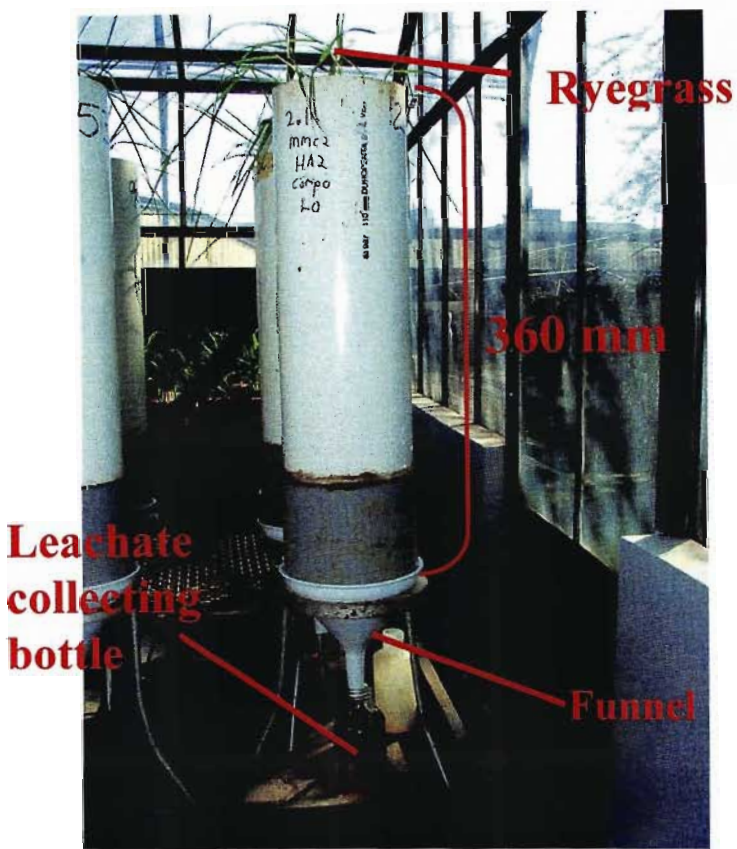
Much of the evidence from the laboratory experiments showed that there is a high concentration of readily available Mn in the EW, thus there exists the risk of groundwater contamination due to leaching of soluble forms of Mn. As the pot experiments (Sections 9.2.1 and 9.2.2) did not investigate the potential of the Mn to leach from the topsoil through subsoil, an additional leaching column experiment was designed to provide insight into this aspect.

The columns used consisted of 360 mm long plastic drain-pipes (i.d. 100 mm) with a fine stainless-steel mesh attached to the base. A plastic funnel was fitted over the base of the pipe to aid in the collection of leachates. A fine glass-wool membrane was placed on the stainless-steel mesh to reduce the loss of sediment during leaching events. The lower 150 mm of the pipes were filled with the Hu subsoil (collected at 400 - 600 mm depth below the Hu topsoil, air-dried and milled to pass through a 2 mm sieve). The pipes were tapped on the ground to promote natural settling that resulted in a bulk density of about  $1.4 \text{ g cm}^{-3}$ . A fine glass-wool membrane was placed on the surface of the subsoil. Topsoil with various combinations of EW, HA and lime (Table 9.2) was then added to fill the next 200 mm of the column (bulk density of about  $1.2 \text{ g cm}^{-3}$ ). As in pot experiment 2, P was added as  $\text{NH}_4\text{H}_2\text{PO}_4$  to achieve a P application level of  $65 \text{ kg P ha}^{-1}$  (for the topsoil layer). About 10 ryegrass seeds were planted, and thinned to four plants 10 days after germination. The

experiment was replicated once. Plate 9.1 presents an image of a column after the plants had been thinned to four per column.

**Table 9.2**      Treatments used in the leaching column experiment

Treatment	Electro-winning waste (g kg <sup>-1</sup> )	Humic acid (g kg <sup>-1</sup> )	Compost (g kg <sup>-1</sup> )	Lime (Mg ha <sup>-1</sup> )
1	20	0	0	0
2	20	20	0	0
3	20	0	20	0
4	20	0	0	5
5	20	20	0	5
6	20	0	20	5
7	0	0	0	0



**Plate 9.1**      The leaching column experimental set-up.

To ensure that the entire mass of soil in the column was moist, about 1 400 mL distilled water was added to each column. This was calculated as the approximate pore volume for the entire soil mass in the column. Thereafter columns were watered, initially, with about

100 mL distilled water every second day, this increasing to about 200 mL as the plants grew larger. No loss of leachate from the base of the column occurred at these watering events.

The columns were leached after 10, 17, 24, 31, 38 and 68 days. The first leaching commenced after the number of plants had been thinned to four per column. About 100 mL of leachate was collected at each leaching event by adding distilled water to the surface of the column in 50 mL increments until the required amount had leached from the base of the column. This typically occurred over a period of about 4 hours. Leachates were collected in small glass bottles and stored at 4 °C until analysis (typically within a day). The pH and EC of the leachates were determined, and the concentrations of Mn and Co in the leachates determined by AAS.

The grass was harvested 38 days after establishment (H1) and again at 68 days (H2). The harvesting and analysis of foliage was conducted as described previously, though in this instance only the concentrations of Mn and Co were determined. Due to the lack of comprehensive replication ( $n = 2$ ) the data were not statistically analysed. In addition this investigation was only conducted to observe the likely trends so that a clearer understanding of the likely fate of soil applied EW could be obtained with respect to some of the treatments applied.

### 9.3 Results and discussion

#### 9.3.1 Effect of slag

##### 9.3.1.1 *Pot experiment 1*

The yield of ryegrass grown in the Hu soil was higher than for the Lo, regardless of SS application rate (Table 9.3; Plate 9.2). In the Lo soil, the yield of ryegrass increased by about 61% from the control at an SS application rate of 60 g kg<sup>-1</sup>, then decreased sharply up to a rate of 480 g kg<sup>-1</sup> (Figure 9.1). In the Hutton soil, the highest yield was achieved at a SS application rate of 120 g kg<sup>-1</sup>, which was not significantly different ( $p > 0.05$ ) from the 60 and 240 g kg<sup>-1</sup> treatments. The yield of ryegrass grown in the Hu soil treated with SS at a rate of 30 g kg<sup>-1</sup> was also higher (3.88 g pot<sup>-1</sup>) than the control (3.19 g pot<sup>-1</sup>),

though the difference was not significant ( $p > 0.05$ ). The lowest yield in both soil types was at the highest SS application rate, though the yield of ryegrass in the Lo soil was significantly lower ( $p < 0.05$ ) than in the Hu soil.

**Table 9.3** Mean total yield ( $\pm$  SE;  $n = 3$ ) of ryegrass grown in either a Longlands or Hutton soil treated with slag from the Samancor Mn-smelter at rates of 0, 30, 60, 120, 240 and 480 g kg<sup>-1</sup>

Soil	Application rate (g kg <sup>-1</sup> )	Yield $\pm$ SE (g pot <sup>-1</sup> )
Longlands	0	0.86 $\pm$ 0.12ef <sup>†</sup>
	30	1.40 $\pm$ 0.02de
	60	1.40 $\pm$ 0.09de
	120	1.13 $\pm$ 0.08de
	240	0.46 $\pm$ 0.20fg
	480	0.14 $\pm$ 0.12g
Hutton	0	3.19 $\pm$ 0.29c
	30	3.88 $\pm$ 0.51bc
	60	4.86 $\pm$ 0.57a
	120	4.89 $\pm$ 0.44a
	240	4.34 $\pm$ 0.82ab
	480	1.52 $\pm$ 0.34d

<sup>†</sup> Letters that are different indicate significant differences between means (LSD<sub>5%</sub>: leaf yield = 0.61; coefficient of variation = 6.6%).

The interactive effect of SS application rate and soil type on the yield of ryegrass was highly significant ( $F_{5,22} = 11.12$ ;  $p < 0.001$ ), as were the individual effects of SS application rate ( $F_{5,22} = 32.90$ ;  $p < 0.001$ ) and soil type ( $F_{1,22} = 576.87$ ;  $p < 0.001$ ).

The concentrations of Ca, Mg, K, N, P and S tended to be within the adequate range for ryegrass (Appendix 9.1). There was generally a decrease in the concentrations of these elements from H1 to H2. Sodium concentrations of the ryegrass (Appendix 9.1) typically increased with an increase in SS application rate up to 240 g kg<sup>-1</sup>, decreasing thereafter. There was also a decrease from H1 to H2 in both soils.

The Cu concentrations of ryegrass grown in the Lo soil were generally below the critical limit for ryegrass for H1, but within the adequacy range for H2 (Appendix 9.2). In the Hu soil the concentrations were within the adequate range, with an increase noted as SS

application rate increased for H1. The Cu concentrations at H2 were generally similar for all treatments. Iron concentrations were all higher than the adequate range for both harvests. The Fe concentrations at H1 were also higher than for H2 (Appendix 9.2).

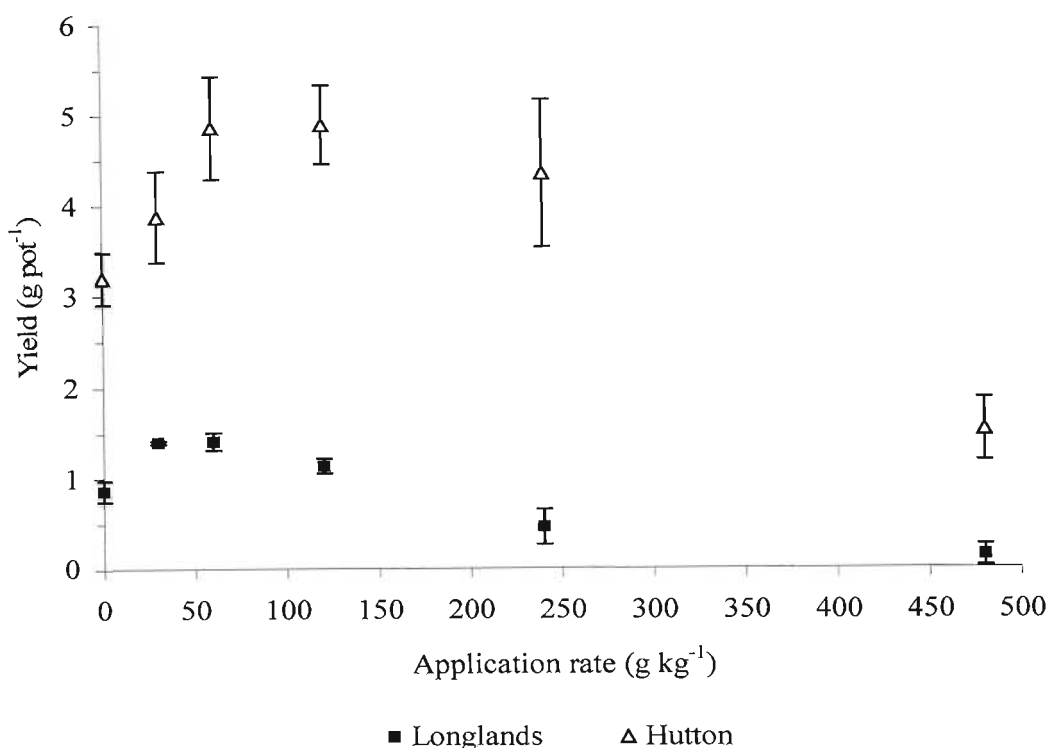


**Plate 9.2** Growth of ryegrass (6 weeks) in (a) Longlands soil and (b) Hutton soil treated with slag at rates of 0, 30, 60, 120, 240 and 480 g kg<sup>-1</sup> (from left to right in each image). The height of each pot is 110 mm.

Zinc concentrations tended to be within the adequacy range for both soil types and both at harvests (Appendix 9.2). Nickel and Pb concentrations were below detection at H1, with increases in both metals for H2, regardless of soil type, though concentrations were still low.

Manganese concentrations increased after the addition of SS in both soil types (Appendix 9.2). In the Lo soil, the highest Mn concentrations were in the 30 and 60 g kg<sup>-1</sup> treatments, for both H1 and H2 (Appendix 9.2). There were also increases in Mn concentrations from H1 to H2 for all SS application rates and in the control soil. In the Hu soil, Mn concentrations increased with an increase in SS application rate for H1. The concentration

of Mn also increased from H1 to H2 in the Hu soil. The highest Mn concentrations, in the Hu soil, were measured in ryegrass grown in  $240 \text{ g kg}^{-1}$  SS treatment at H2. Cobalt concentrations were below detection for all treatments and thus are not reported.



**Figure 9.1** Mean total yield ( $\pm$  SE) of ryegrass grown in either a Longlands or Hutton soil treated with slag from the Samancor smelter at rates of 0, 30, 60, 120, 240 and  $480 \text{ g kg}^{-1}$ .

Addition of SS to both the Lo and Hu soil improved the yield of the ryegrass, but the application rate at which the effect became negative varied for each soil. In the Lo soil maximum yield was achieved at between 30 and  $120 \text{ g kg}^{-1}$ , while in the Hu soil it was between 60 and  $240 \text{ g kg}^{-1}$ . This was probably due to the SS improving soil pH while supplying some nutrients, such as Ca. In the Lo soil it was likely that Cu and Zn deficiencies, especially at the high SS application rates, were the cause of the reduction in yield. The low N concentrations were probably also responsible for the generally low yields in this soil. The high Mn concentrations of the grass grown in the Lo soil at the low SS application rates (notably the 30 and  $60 \text{ g kg}^{-1}$ ) were cause for concern as they exceeded the range reported as being adequate for ryegrass (Appendix 9.2). Under field conditions this grass may be consumed by foraging animals leading to toxicity in those animals. The high Ca concentrations may have ameliorated the negative impact of such high Mn

concentrations. Some authors indicate that the Ca:Mn ratio in the leaf tissue is important for the growth of plants. Hue *et al.* (2001) found that a Ca:Mn ratio of  $> 50$  was necessary for normal growth of soybean, while Hue and Mai (2002) suggested that a ratio of  $> 25$  was critical for the growth of watermelon. This was not the case in this instance. The Ca:Mn ratio varied from 3.3 to 82.2 and 1.1 to 20.5 for H1 and H2, respectively. There was also no correlation between these ratios and the yield of ryegrass.

El-Jaoual and Cox (1998) indicated that high concentrations of Si might protect plants against Mn toxicity. Given that the slag is siliceous in nature, it is possible that there were increased levels of Si in the ryegrass, though this was not investigated here. The exact mechanism for the amelioration of Mn toxicity by Si is not clear, but may be related to a number of factors, including reduced Mn uptake from the soil, reduction in root to shoot transport of Mn, homogeneous distribution of Mn throughout the leaf tissue (as opposed to concentrated Mn spots) and improved cellular compartmentalization of Mn in leaf tissue (El-Jaoual and Cox, 1998).

While the Mn concentrations of ryegrass grown in the Hu soil were generally not as high as those found in the ryegrass grown in the Lo soil, it is likely that a similar mechanism was responsible for protecting the plants against Mn toxicity. The Hu soil also had a higher CEC (Chapter 6) resulting in an increase in the sorption of soluble Mn from the soil solution, reducing the amount available for plant uptake. It is clear, however, that for both soil types, the addition of SS can lead to elevated Mn levels in plant tissue. While the SS has a high acid-neutralising capacity, a consequence is dissolution of the slag, releasing Mn into the soil solution. Further soil acidification by the plant roots is likely to continue to promote SS dissolution thus releasing more Mn. It appears that the acetic acid-extractable amounts of Mn measured in the slag (Chapter 6) may more closely mimic rhizosphere effects in vegetated soils, especially at the lower application rates of SS.

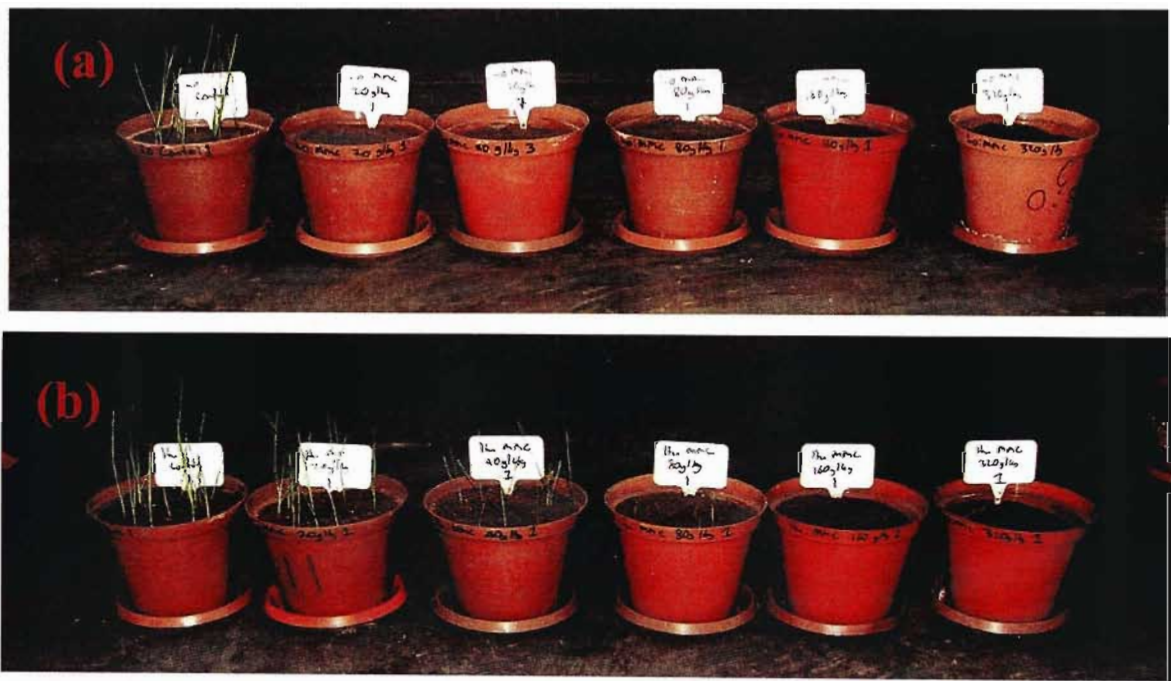
### 9.3.2 Effect of electro-winning waste

#### *9.3.2.1 Pot experiment 1*

None of the grass grown in the EW-treated Lo soil or the Hu soil treated with 80, 160 and 320 g kg<sup>-1</sup> EW survived for long beyond germination (Plate 9.3), so no growth data are



available. In the Hu soil the ryegrass survived at EW application rates of 20 and 40 g kg<sup>-1</sup> (Table 9.4). The yields of ryegrass from each harvest were similar to the control soil, but were higher for H2 than for H1 at EW application rates of 20 and 40 g kg<sup>-1</sup>. At H1, the yield was highest at an EW application rate of 20 g kg<sup>-1</sup>, while the control soil and 40 g kg<sup>-1</sup> treatments were similar. By H2 the highest yield was found at the highest EW application rate, the yield being about 4.6 times that of the control. The high yields of grass grown in the EW-treated soil at H2 resulted in high total yields.



**Plate 9.3** Growth of ryegrass (6 weeks) in (a) Longlands soil and (b) Hutton soil treated with electro-winning waste at rates of 0, 20, 40, 80 160 and 320 g kg<sup>-1</sup> (from left to right in each image). The height of each pot is 110 mm.

**Table 9.4** Mean yield from H1 and H2 and mean total yield ( $\pm$  SE;  $n = 3$ ) of ryegrass grown in either a Hutton soil treated with electro-winning waste from MMC at rates of 0, 20 and 40 g kg<sup>-1</sup>. Yield expressed as g pot<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	H1		H2		Total	
	Mean	$\pm$ SE	Mean	$\pm$ SE	Mean	$\pm$ SE
0	1.74	0.21	1.45	0.15	3.19	0.29
20	2.69	0.11	4.83	0.62	7.52	0.52
40	1.99	0.16	6.60	0.22	8.60	0.34



Nutrient analysis showed that Ca and Mg concentrations were within the adequate range reported for ryegrass, for both harvests (Appendix 9.3). Potassium concentrations increased with an increase in EW application rate at H1 but remained in the adequate range for ryegrass (Appendix 9.3). There was a marked decrease in K concentrations for the EW treatments at H2, with K concentrations below the critical limit. This may have been a dilution effect due to the high yield of these treatments at H2. The N concentrations of the ryegrass grown in the EW-treated soil were higher than that of the control soil, though still below the adequacy range for ryegrass for H1 (Appendix 9.3). By H2, the N concentration of the control and 20 g kg<sup>-1</sup> EW treatment had decreased substantially, but was still elevated in the 40 g kg<sup>-1</sup> EW treatment. Phosphorus concentrations were below the critical limit for H1, decreasing even further by H2, though P deficiency was not visually evident in any of the treatments.

Sulphur concentrations were generally higher than the range reported to be adequate and also increased with an increase in EW application rate for H1 (Appendix 9.3). There was an increase in the S concentration of the ryegrass for the control treatment of H2, but a decrease for the EW treatments.

Cobalt concentrations were below detection for H1, but increased slightly by H2 in the EW treatments (Appendix 9.3). Both Cu and Zn concentrations increased with an increase in EW application rate, with Cu concentrations generally within the adequate range and Zn above the upper limit of the adequate range (Appendix 9.3). Iron concentrations tended to be higher than the reported adequacy range, even in the control soil. There was a decrease in Fe concentrations from H1 to H2. The concentrations of Mn increased sharply with an increase in EW application rate. At H1 the Mn concentrations of the 20 and 40 g kg<sup>-1</sup> EW treatments were about 5 and 20 times, respectively, higher than in the control soil (Appendix 9.3). The Mn concentrations of the ryegrass grown in the control soil and 40 g kg<sup>-1</sup> EW treatment increased markedly from H1 (65.9 and 1312 mg kg<sup>-1</sup> for the control and 40 g kg<sup>-1</sup> EW treatment, respectively) to H2 (327 and 1929 mg kg<sup>-1</sup> for the control and 40 g kg<sup>-1</sup> EW treatment, respectively), while the 20 g kg<sup>-1</sup> treatment remained relatively unchanged (323 and 314 mg kg<sup>-1</sup> for H1 and H2, respectively). As was the case for the SS-treated Hu soil, both Ni and Pb concentrations were below detection at H1, but increased by H2 (Appendix 9.3). Concentrations of these metals in the ryegrass from the control soils

tended to be similar to the EW treatments, suggesting that the waste was not the only contributing factor and that the metals were being released from the Hu soil.

The performance of ryegrass was suppressed at the highest EW application rates for H1. Considering the effect of the EW on the EC of the soils (Chapter 7 and Section 9.3.2.1) it was suspected that salinity was the cause. Keren (2000) and Mills *et al.* (2004) indicated that the exact effects of salinity remain elusive, but that it may cause toxicity (due to specific ion effects) or lead to osmotic stress in the plants. The newly germinated seedlings may have experienced osmotic stress at the high EW application rates, reducing their growth rate. Once the grasses had developed to a point where they were able to overcome the osmotic stress, they grew very well, aided by high levels of available N in the EW-treated soils. It was speculated that the small, fine roots of the newly germinated seedlings were unable to counter the high osmotic potential of the surrounding soil solution. This resulted in a similar effect to dry soil, where the seedling was unable to extract adequate moisture from the soil, this leading to the plant losing turgidity and eventually dying. In addition the high  $\text{NH}_4^+$  concentrations may also have had a toxic effect on the seedlings. The high EC was, however, the likely cause of death of the ryegrass grown at the higher EW application rates ( $> 40 \text{ g kg}^{-1}$ ) and at all EW application rates in the Lo soil. Plate 9.4 shows the salt build-up on the surface of the soils treated with the high rate of EW ( $320 \text{ g kg}^{-1}$ ).

The interaction of Mn with other elements is commonly reported in the literature. For instance, Foy *et al.* (1978), El-Jaoual and Cox (1998), Kabata-Pendias and Pendias (2001) indicated that Mn may interact with Al, Fe, Ca, P, Si and K. Excess Mn may have antagonistic effects on the uptake of Fe, Ca and Mg due to increased competition between these cations. Conversely, increasing the concentrations of these elements may reduce Mn uptake by plants and so reduce toxicity. Although elevated levels of Mn were found in the ryegrass of some treatments, there was no evidence of Mn toxicity in any of these treatments, while the concentrations of other nutrients tended to be within or over the acceptable ranges for ryegrass.



**Plate 9.4** Salt build-up (white residue) on the surface of the (a) Longlands and (b) Hutton soils treated with electro-winning waste at a rate of  $320 \text{ g kg}^{-1}$ .

It has also been suggested that the form of Mn may be important in assessing the potential toxic effect. Hue *et al.* (2001) investigated the effect of various forms of Ca and Mg, including  $\text{CaSO}_4$  and  $\text{MgSO}_4$ , on Mn uptake and toxicity in soybean grown in a Mn-rich Oxisol and found that both sulphate salts were effective at increasing soybean biomass. They speculated that  $\text{Mn}^{2+}$  ions reacted with the  $\text{SO}_4^{2-}$  ions to form neutral ion pairs that were not as toxic as  $\text{Mn}^{2+}$  in solution. It is possible that, in the case of the EW, the manganese existed as these neutral ion pairs and so was not as toxic to the plants as the unassociated species might be. This would, in part, explain the apparent lack of toxicity symptoms exhibited by the ryegrass grown in the EW-treated soils from the preliminary experiment, even though Mn concentrations were exceptionally high. It is also possible that the ryegrass exhibited a high tolerance to high levels of soil and tissue Mn. Arienzo *et al.* (2003) reported that ryegrass tolerated high levels of Cu, Zn and Pb when grown in a contaminated soil. While they did not investigate Mn tolerance, it does suggest that ryegrass may be tolerant of elevated metal concentrations in the soil. Paschke *et al.* (2005) investigated the Mn toxicity thresholds for some grasses used in restoration of contaminated and derelict land. They used various indicators as measures of Mn toxicity in the plants. Of these, the  $\text{PT50}_{\text{shoot}}$  (concentration of Mn in plant shoots that result in a 50%

reduction in plant biomass) is perhaps the most useful as a comparison for this investigation. They report values from 41 528 to 120 082 mg kg<sup>-1</sup> for five different grass species. While none of these grass species included ryegrass, it does suggest that grasses may exhibit a very high tolerance to high Mn concentrations.

### 9.3.2.2 *Pot experiment 2*

#### 9.3.2.2.1 *Incubation experiment*

Appendix 9.4 presents the results from the ‘mini’ incubation experiment. As was reported in Chapter 8, the addition of EW tended to lower the pH of the soil. Addition of lime increased the pH of the EW-treated soils relative to the unlimed EW-treated soils. Overall the HA treatments had a higher pH than the compost treatments. The EC and Mn concentrations increased with an increase in EW application rate, though the effect of the other treatments was not marked.

#### 9.3.2.2.2 *Pot experiment*

The highest total yield (12.21 g pot<sup>-1</sup>) was measured in the compost treatment with lime added at 10 Mg ha<sup>-1</sup> and an EW application rate of 40 g kg<sup>-1</sup> (Table 9.5). This was almost double the total yield of the control treatment at the 40 g kg<sup>-1</sup> EW application rate (6.36 g kg<sup>-1</sup>), but was only slightly higher than the compost and lime (applied at 0 and 5 Mg ha<sup>-1</sup>) for the 40 g kg<sup>-1</sup> (10.90 and 10.32 g pot<sup>-1</sup>, respectively) and the humic acid with no lime at the 40 g kg<sup>-1</sup> EW application rate (10.12 g pot<sup>-1</sup>). Generally, for each organic matter and lime combination, there was an increase in total yield as the application rate of EW increased (Table 9.5). The addition of compost improved the yield of the ryegrass relative to the HA-treated soils and the control EW-treated soils for H1. This was not evident for H2, except at the highest EW application rates.

**Table 9.5** Mean yield from Harvest 1 (H1) and Harvest 2 (H2) and total yield ( $\pm$  SE;  $n = 3$ ) of ryegrass grown in a Hutton soil treated with electro-winning waste (EW) from MMC at rates of 0, 10, 20 and 40 g kg<sup>-1</sup> and organic matter (either humic acid or compost) at 0 or 20 g kg<sup>-1</sup> with the organic matter treatments receiving lime at rates of 0, 5 and 10 Mg ha<sup>-1</sup>

EW application rate (g kg <sup>-1</sup> )	Treatment	Yield (g pot <sup>-1</sup> )					
		H1		H2		Total	
		Mean	$\pm$ SE	Mean	$\pm$ SE	Mean	$\pm$ SE
0	20 g kg <sup>-1</sup>	1.42	0.27	1.24	0.11	2.66	0.38
10	humic acid	2.43	0.16	1.68	0.13	4.11	0.23
20	+ 0 Mg ha <sup>-1</sup>	2.32	0.68	2.97	1.46	5.30	1.42
40	lime	2.05	0.62	8.07	1.36	10.1	1.98
0	20 g kg <sup>-1</sup>	1.73	0.13	1.47	0.06	3.21	0.19
10	humic acid	2.69	0.13	1.76	0.11	4.45	0.23
20	+ 5 Mg ha <sup>-1</sup>	2.62	0.46	2.77	0.62	5.40	0.53
40	lime	2.09	0.14	6.78	0.25	8.87	0.36
0	20 g kg <sup>-1</sup>	1.93	0.03	1.73	0.30	3.66	0.30
10	humic acid	2.36	0.10	2.03	0.35	4.39	0.38
20	+ 10 Mg ha <sup>-1</sup>	2.59	0.06	3.10	0.30	5.69	0.26
40	lime	2.13	0.13	6.73	0.70	8.86	0.82
0	20 g kg <sup>-1</sup>	2.51	0.05	1.61	0.13	4.12	0.13
10	compost	3.56	0.23	2.36	0.11	5.92	0.33
20	+ 0 Mg ha <sup>-1</sup>	3.87	0.34	2.98	0.29	6.85	0.05
40	lime	4.22	0.25	6.68	0.32	10.9	0.55
0	20 g kg <sup>-1</sup>	2.46	0.18	1.64	0.09	4.10	0.14
10	compost	2.91	0.53	1.96	0.27	4.88	0.80
20	+ 5 Mg ha <sup>-1</sup>	3.59	0.36	3.37	0.68	6.96	0.39
40	lime	3.57	0.47	6.75	3.52	10.3	3.05
0	20 g kg <sup>-1</sup>	2.43	0.08	1.81	0.20	4.24	0.27
10	compost	3.06	0.09	2.12	0.39	5.18	0.32
20	+ 10 Mg ha <sup>-1</sup>	3.49	0.19	3.41	0.86	6.90	0.95
40	lime	3.10	0.43	9.11	0.81	12.2	0.93
0	Control	1.40	0.17	1.16	0.07	2.56	0.14
10	(No organic	2.32	0.12	1.65	0.17	3.97	0.30
20	matter or	2.75	0.19	2.68	0.14	5.43	0.29
40	lime)	1.49	0.40	4.88	0.62	6.36	1.00
LSD <sub>5%</sub>		1.34		1.30		0.51	

The yields of ryegrass for each individual treatment from H1 and H2 tended to be similar at an EW application rate of 20 g kg<sup>-1</sup>, but generally decreased at the lower EW application rates (0 and 10 g kg<sup>-1</sup>). At the highest EW application rate (40 g kg<sup>-1</sup>) the yield from H2

was consistently higher than the equivalent treatment at H1. For instance, at an EW application rate of  $40 \text{ g kg}^{-1}$  with compost and lime (at  $10 \text{ Mg ha}^{-1}$ ) the yield increased from  $3.10$  to  $9.11 \text{ g pot}^{-1}$ , and in the control soil (no organic matter or lime) the yield increased from  $1.49$  to  $4.88$ . The higher total yields of the high EW treatments were attributed to the marked increases in yield at H2 for these treatments. There were significant overall interactive effects of EW application rate and organic matter/lime treatment on the yield of ryegrass for H1 ( $F_{18,54} = 2.92$ ;  $p = 0.001$ ) and total yield ( $F_{18,54} = 2.45$ ;  $p = 0.006$ ) and a marginally significant interactive effect for H2 ( $F_{18,54} = 1.80$ ;  $p = 0.05$ ).

The individual effects of either EW application rate or organic matter/lime application rate were also all significant for the yields from both harvests and total yield (Appendix 9.5). Generally, the Ca concentrations tended to be higher in the compost and control treatments than in the humic acid treatments, but did not seem to be associated with the lime application rate (Appendix 9.6). There was also a decrease in Ca concentrations of the ryegrass, for most treatments, from H1 to H2, though concentrations were typically within the adequate range reported for ryegrass (Appendix 9.6). Magnesium followed a similar trend to Ca though the concentrations were lower. The Mg concentrations were also typically within the adequacy range reported for ryegrass (Appendix 9.6). Potassium concentrations of the HA-treated soils tended to be higher than for the other treatments, attributed to the high K concentrations of the HA (13%; Appendix 8.5).

The P concentrations of ryegrass tended to decrease with an increase in EW application rate for H1. By H2 there were clear decreases in P uptake as EW application rate increased for the different organic matter and lime treatments (Appendix 9.6). At H1, P concentrations were within or over the adequate range given by Miles (1994), but tended to be below the critical limit by H2 for ryegrass grown at the high EW application rates. Nitrogen concentrations of the ryegrass from H1 increased with an increase in EW application rate, but did not appear to be markedly influenced by any of the other treatments (Appendix 9.6). There was a marked drop in N concentrations of the ryegrass from H1 to H2. At H2 the ryegrass grown at the low EW application rates tended to have similar N concentrations, while at the highest EW application rate ( $40 \text{ g kg}^{-1}$ ) the N concentration was higher than at the low rates.

Copper concentrations of the ryegrass increased with an increase in EW application rate, but did not appear to be associated with the other treatments (Appendix 9.7). There was a decrease in Cu concentrations from H1 to H2, though the trend seen for H1 generally remained the same. Iron concentrations (Appendix 9.7) reflected those reported in the first experiment (Appendix 9.3) and no discernible pattern was evident. There was, however, a general decrease in Fe concentration from H1 to H2 (Appendix 9.7). The concentrations of Mn in the ryegrass increased with an increase in EW application rate regardless of the organic matter or lime treatments. The highest Mn concentration ( $359 \text{ mg kg}^{-1}$ ) was measured in the ryegrass grown in the compost (without lime) treatment at the highest EW application rate (Appendix 9.7), suggesting that the compost increased the availability of Mn from the EW.

The addition of HA generally decreased Mn concentrations of the ryegrass, with additional lime further reducing Mn uptake, compared to the control treatments. The same was also evident in the compost-treated soils. There was generally an increase in Mn uptake by the ryegrass for H2 regardless of treatment. The highest Mn concentrations for H2 tended to be in the control and compost (without lime) treatments followed by the HA (without lime treatment). This suggests that the addition of lime can reduce Mn uptake by the ryegrass. As was noted in the first experiment, Zn concentrations were high and tended to increase with an increase in EW application rate. In almost all cases for both harvests, the Zn concentrations were higher than the adequate range (Appendix 9.7).

The Mn concentrations of the ryegrass grown in the EW-treated soils without any other amendments were lower than found in the preliminary experiment at similar application rates of EW. It was suspected that the addition of the P-fertiliser used in the second experiment resulted in the formation of Mn-P compounds, reducing Mn availability. Foy *et al.* (1978) and El-Jaoual and Cox (1998) indicated that Mn toxicity symptoms may be reduced in Mn-rich soil when P-fertiliser is added due to the formation of precipitates, either in the plant roots or in the soil solution. The interaction between manganous sulphate and phosphoric acid at varying Mn:P ratios and pH was investigated by Heintze (1968) who found that Mn-P precipitates (identified as manganese ortho-phosphate) would form, regardless of pH, if the Mn:P ratio was 1. Where there were large initial concentrations of Mn relative to P, poorly defined Mn-P compounds formed. Generally, Mn concentrations decreased sharply above a pH of 6.5 to 7.0, depending on the Mn:P ratio. Heintze (1968)



also reported that Mn uptake by oats, grown in a soil with added Mn, was reduced after the addition of a phosphate fertiliser. This served to show that application of phosphate compounds may be beneficial in reducing Mn availability in the waste. It probably also masked some of the other treatment effects that were the primary focus of the investigation (effects of OM and lime additions). As mentioned earlier, some authors report that the Ca:Mn ratio of the plant tissue is an important yield-determining factor. No relationship was found between the yield of the ryegrass for either H1 or H2 and the Ca:Mn ratios at each respective harvest (for pot experiment 2), suggesting that it was not a critical factor for ryegrass grown under these experimental conditions.

The concentrations of most elements decreased from H1 to H2, except in the case of Mn. It is expected that, in a pot experiment with repeated harvests, nutrients would become depleted due to uptake by the plants. Unless additional nutrients are added or there is dissolution of compounds containing these nutrients, it is unlikely that there would be an increase over time. Considering that only an ammonium phosphate fertiliser was used at the start of the experiment, the increase in Mn concentrations from H1 to H2 was probably due to the dissolution of Mn-containing compounds. In Chapter 8 it was shown that at high application rates of EW, the presence of organic matter may, in part, promote the solubility of Mn in soil-applied waste. However, the effect of OM on Mn availability was not as clear at the low EW application rates. Furthermore, data from the 'mini' incubation experiment suggested that addition of organic matter was less of a driver on Mn availability than pH at these lower EW application rates. The pot experiment further supported the argument that organic matter was not a primary factor in the release of Mn from the waste at low application rates, as the Mn concentrations of the controls soil tended to be similar to or higher than the equivalent OM-treated soils. In this case it was considered that pH was the principal factor driving the release of Mn from the waste. As indicated earlier some of the Mn from the EW applied to the soil was bound as insoluble phosphate compounds, but acidification of the soil may have resulted in the dissolution of these compounds (and also Mn bound in the minerals of the EW) releasing the Mn for plant uptake. This acidity may have been generated from three likely sources, namely nitrification, decomposition of organic matter and  $H^+$  exchange from plant roots during nutrient uptake. It has been previously established that addition of EW promotes the generation of acidity due to nitrification of  $NH_4^+$  in the waste (Chapter 7). Furthermore, all pots had additional  $NH_4^+$  added as fertiliser. Siman *et al.* (1971) reported that ammonium sulphate additions to an



acid, red-basaltic soil, rich in Mn, increased the uptake of Mn by French beans. They attributed the increase in Mn availability to increased acidity due to nitrification processes.

9.3.2.3 *Leaching column experiment*

The mean yield and Mn concentrations of ryegrass from H1 and H2 are given in Table 9.6. Cobalt concentrations were below measurable limits for all treatments and harvests. The highest ryegrass yields at H1 were measured in the HA and compost-treated soils that did not have lime added (Treatments 2 and 3, respectively; Table 9.6). The yields of the ryegrass grown on the HA and compost-treated soils with 5 Mg ha<sup>-1</sup> lime added (Treatments 5 and 6, respectively) were next highest, but only slightly higher than that of the ryegrass grown in soil only treated with EW (Treatment 1) and EW plus lime (Treatment 4).

**Table 9.6** Mean yield (n = 2) and mean Mn concentrations (n = 2) of ryegrass grown in the leaching columns with various combination treatments of electro-winning waste, organic matter and lime for Harvest 1 (H1) and Harvest 2 (H2). Treatment descriptions are given in Table 9.2

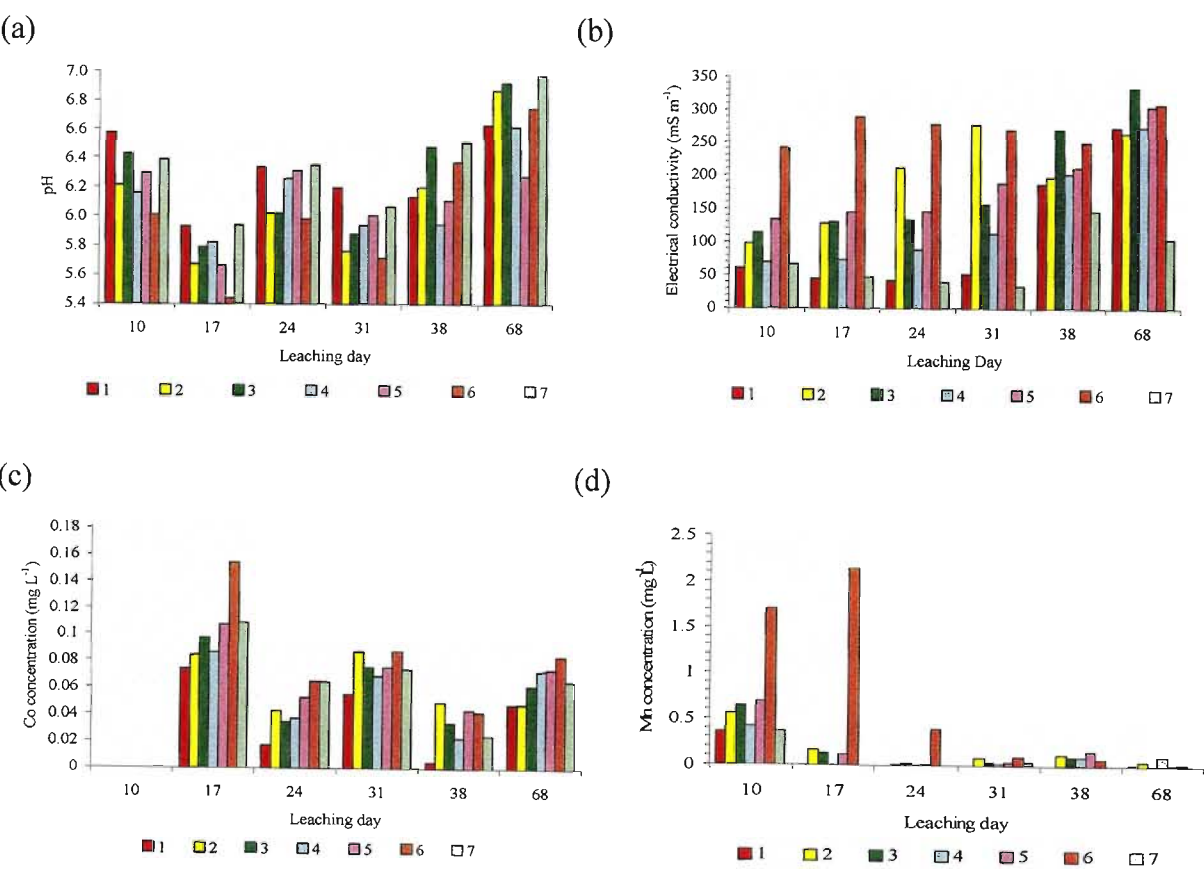
Treatment	Yield		Mn	
	H1	H2	H1	H2
	----(g pot <sup>-1</sup> )----		---(mg kg <sup>-1</sup> )--	
1	2.59	3.53	98.0	268
2	4.13	7.09	82.1	187
3	4.35	5.30	95.7	216
4	2.50	5.71	111	99.7
5	2.63	6.05	58.8	121
6	2.82	5.60	60.6	83.2
7	1.86	1.44	93.5	264

bd below detection.

The yield of the ryegrass grown in the untreated Hu soil (Treatment 7) was lowest at H1, decreasing further by H2, where it was again the lowest yielding treatment. There was an increase for all the other treatments at H2. The highest yield was measured for Treatment 2, followed by Treatment 5, the HA-treated soils. The yield of ryegrass grown in Treatment 3, 4 and 6 were similar, with slightly higher yields measured in the lime treatments (4 and 6) than the unlimed compost treatment (3).

The lowest Mn concentrations were measured in the limed organic matter treatments (5 and 6; 58.8 and 60.6 mg kg<sup>-1</sup>, respectively), and the highest for H1 was in the EW and lime treatment (Treatment 4; 111mg kg<sup>-1</sup>). The other treatments were generally similar. There was a marked increase in the Mn concentrations of the ryegrass, for most treatments, by H2. The exceptions were Treatment 4 that decreased by about 10% and Treatment 6, which only increased by about 27%. The other treatments increased by between 2 and 3 fold, reflecting a trend similar to that seen in the previous experiments (Sections 9.3.1.2 and 9.3.2.2) The highest Mn concentrations were measured in ryegrass grown in Treatments 1 and 7, that were of a similar magnitude.

There was generally an overall increase in pH for most of the treatments over time (Figure 9.2a).



**Figure 9.2** The (a) pH and (b) electrical conductivity, and concentrations of (c) Co and (d) Mn, of leachate collected from leaching columns. Treatments 1 to 7 are described in Table 9.2.

The EC levels generally increased over time for all treatments (Figure 9.2b). Treatment 6 had the highest EC at Day 10 ( $241 \text{ mS m}^{-1}$ ), increasing to  $307 \text{ mS m}^{-1}$  by Day 68. All the other treatments were below  $150 \text{ mS m}^{-1}$  at Day 10, but increased to over  $250 \text{ mS m}^{-1}$ , except for Treatment 7 that remained below  $150 \text{ mS m}^{-1}$ , clearly indicating that the addition of EW influences the EC of the leachate. This supports the finding presented in Section 7.3.2.2, regarding the effect of adding EW to soils on the EC of those soils. The effect of each treatment was more variable. However, the OM-treated soils (Treatments 2, 3, 5 and 6) had higher EC values than the other Treatments (1, 4 and 7) from Day 10 to Day 31. By Day 38, however, this was no longer evident. This suggests that, at least initially, the OM contributed to the EC of the leachate.

The concentrations of Co in the leachates were all below measurable limits at Day 10, but had increased considerably by Day 17 ( $< 0.15 \text{ mg L}^{-1}$ ; Figure 9.2c). There was no distinct trend over time, except for a general decrease in Co concentrations for all treatments. It was noted that the highest Co concentrations were measured in Treatment 6, which also had the highest EC values. This trend was also noted for the concentrations of Mn in the leachates (Figure 9.2d). The Mn concentrations were highest for Treatment 6 at Days 10, 17, 24 and 31, though there was a sharp decrease from Day 17 to 24 ( $2.14$  to  $0.38 \text{ mg L}^{-1}$ ). It was also noted that the Mn concentration of the ryegrass foliage for Treatment 6 was generally lower than the other treatments at both H1 and H2. While the Mn concentrations of the other OM treated soils (Treatments 2, 3 and 5) were not as high as that of Treatment 6, they were higher than the treatments without OM added (Treatments 1, 2 and 7), at Day 10. The Mn concentrations decreased for all these treatments by Day 17, though the OM-treated soils still had higher Mn concentrations than the soils without OM added. The Mn concentrations remained low after this. Ross (1994) indicates that soil solution concentrations of  $0.01$  and  $0.1$  to  $10 \text{ mg L}^{-1}$  Co and Mn, respectively, can be considered to be toxic for soil organisms. This suggests that Co may be problematic, though this was not as clear for Mn.

These data showed that generally there was not a substantial amount of leaching of Mn through a simulated soil profile, and that there was a decrease over time. This suggests that under certain conditions the EW can be applied to land, though it is probable that soil type and depth will play a major role in determining the amount of leachate that moves through a given soil profile. If, for instance, the Lo soil was used, it is likely that most of the Mn

from the EW would leach readily. There was also evidence that salinity of leachate may increase, and Co concentrations of the leachate may lead to toxicity problems in biota that contacts this leachate.

## 9.4 Conclusions

### 9.4.1. Effect of slag

Low application rates of SS may be beneficial for plant growth, probably due to slight improvements in plant nutrient availability and improved soil pH. At high SS application rates elevated pH and low nutrient availability (notably Cu) may have been the cause of the reduction in the yield of ryegrass. Elevated concentrations of Mn were also measured in some treatments, indicating that dissolution of the SS was occurring and that the Mn was in an available form in the soil. While the elevated Mn concentrations did not appear to negatively impact on the yield of the ryegrass, it may limit the application of SS to land if the land is to be used for forage or food crops due to potential toxicity effects in the consumers of the crops (El-Jaoual and Cox, 1998; Fraga, 2005).

There appears to be limited potential for the disposal of SS to land. The characteristics of the soil determine the application rate that is possible. It is clear that in an unbuffered soil, such as the Lo, only low rates of SS are possible. In a more strongly buffered soil, like the Hu, higher application rates are feasible. Based on ryegrass yields an upper limit of between 120 and 240 g kg<sup>-1</sup> (288 and 576 Mg ha<sup>-1</sup>) is possible although there exists the risk of Mn toxicity, even though toxicity symptoms were not evident in this study.

### 9.4.2 Effect of electro-winning waste

It is clear that high rates of EW waste have a negative impact on ryegrass growth. It appears that high salinity is the cause, especially for seedlings that cannot overcome the osmotic stress. Low application rates of EW improve the growth of ryegrass, probably due to improved N nutrition, but also other nutrients. Combination treatments of lime and organic matter increased the yield of ryegrass grown in EW-treated soils. Of concern, even at the low EW application rates, is the high Mn uptake by the plants grown in treated soil. While the addition of lime helped reduce Mn availability in the EW-treated soils (due to

increases in pH and the ameliorating effect of Ca on Mn toxicity), there was evidence to indicate that the addition of phosphate-rich compounds was more effective at reducing Mn uptake by plants. It was speculated that the P-compounds complexed the Mn in an unavailable form, though this requires further investigation. Leaching of the soluble Mn may also reduce Mn uptake by plants grown in EW-treated soil, though this may lead to contamination of groundwater resources, limiting the use of this option. Data from this investigation suggest that, generally, leaching of Mn will be limited, though this was only tested at the lowest EW application rate and on a single soil type. Cobalt leaching may potentially be a problem. Further investigations are necessary to determine the impact over a wider range of conditions before a recommendation for field-testing can be made.

Like the SS, there appears to be limited potential for the disposal of EW to land. Disposal of the EW to a sandy soil is not recommended as even at low rates seedlings are killed. In the Hu soil application is limited to 20 to 40 g kg<sup>-1</sup> (24 to 48 Mg ha<sup>-1</sup>) based on the plant survival. This is in line with the limits for disposal suggested in Chapter 8. As with the SS, Mn is probably the primary element of concern and this may limit the application rate even further, unless additional ameliorating agents are added (such as P-compounds).

## CHAPTER 10

### GENERAL DISCUSSION AND CONCLUSIONS

#### 10.1 Introduction

The initial objective of this investigation was to investigate the phytoremediation of mineral processing wastes, with the emphasis on metal hyperaccumulation. It became apparent that this technology was not suitable for use at the sites selected. This prompted a reconsideration of the original project outlines and objectives, effectively dividing the work into two distinct avenues of thought. Consideration was given to revegetation of the metalliferous tailings at Pering Mine, while land disposal of Mn-rich processing wastes from Samancor and MMC was investigated as a possible means of disposing of these wastes. Although the general approaches to each technology differed, consideration of similar issues was required for successful implementation of each technology. The revegetation of tailings is primarily aimed at reducing the dispersal of contaminants into the surrounding environment. Land disposal aims to discard a waste to land without causing negative impacts to the environment, using the soil (and plants) to assimilate the waste. In both cases the final objective is to produce a result that does not degrade the environment and offers a solution to remediate an existing waste problem. Both technologies require that the risks be assessed, that a strategy be developed and implemented that deals with the specific waste problem, that the success of the amelioration approach be assessed, and that this is monitored to ensure there are no long-term negative impacts. The following discussion will highlight the key findings of each investigation and recommend avenues for further research.

#### 10.2 Revegetation of tailings from Pering Mine

The tailings at Pering Mine had high alkalinity, high acid-neutralising capacity and elevated concentrations of certain trace elements, notably Zn. The tailings were also nutrient-poor and, as the mine was located in a relatively arid environment, water availability was limited. Other by-products (such as biosolids) that could have been used to improve the substrate properties were not readily available thus ameliorants were limited to the use of inorganic fertilisers. The use of plants adapted to grow in this environment was

considered a feasible strategy as it could reduce long-term inputs required to sustain the system.

Therefore, seed of various grass species, predominantly from the mine area, were collected and grown in the tailings with various rates of inorganic fertiliser. It was clear that the addition of fertiliser promoted the establishment of some grasses, and that grasses endemic to the mine area may be better suited to revegetate the tailings dam. Species tested here that proved to be successful were *C. ciliaris*, *D. eriantha* and *E. superba*, while *F. africana* and *C. plurinodis* could also be used to improve diversity. A drawback of the approach used was that seed collection was required. This is notoriously difficult, as different species flower and set seed at different times in the flowering season, and some species require that the seed undergo environmental conditioning to break dormancy. As the latter requirement is often poorly understood, finding the appropriate triggers may be difficult. Of course it is also necessary to collect enough seed for a viable revegetation programme. Some of the species tested here are commercially available, both in seed form and as seedlings (grass plugs), which may be the quickest approach to establish an initial cover. Collection and propagation of other species may require the establishment of a nursery where they can be grown in large numbers for use in a revegetation programme.

It was found that direct germination of seed in the tailings was not likely to be feasible. As such, seedlings were used to establish plants in the pots. The rooting media can thus be treated with a slow release fertiliser and water sorbing 'gels', improving the likely success when establishing the seedlings. This approach is, unfortunately, a time consuming and costly approach to implement at the field scale.

Both laboratory analyses and pot experiments highlighted that certain nutrient deficiencies were likely. Nitrogen and P are typically applied when revegetating derelict sites. The application of P-fertiliser may have limited influence as the tailings had a very high capacity to immobilise P. The rates of P required to overcome this may be excessively high and not practical. For instance, based on the P-sorption isotherm data, to achieve residual soil-solution P values of 0.05 and 0.2 mg L<sup>-1</sup>, P application rates of about 255 and 510 kg ha<sup>-1</sup>, respectively will be required (assuming an incorporation depth of 0.3 m and a bulk density of 1.7 g cm<sup>-3</sup>). This further supports the argument that locally endemic species,

adapted to the naturally calcareous soils found in the surrounding environment, be used to revegetate the tailings dam.

Although not investigated here, some consideration must be given to establishing larger herbaceous and woody species in the tailings. This, however, can be better achieved at the field scale, as establishing large plant species in pots is not particularly reflective of the potential of the roots of such species to explore the larger substrate volume. The establishment of legumes is also likely to promote N-cycling in the tailings.

An attempt to promote metal uptake by grasses grown in the tailings failed. The use of organic chelating agents does not appear to be an appropriate technology for use at this site, and is probably not necessary with respect to any revegetation programme. However, there may be some value in considering the effect of organic acids on metal mobilisation. Once vegetation has been established, there is likely to be an increase in the acid-generating potential, due to root action and organic material decomposition. Under these conditions it may be useful to investigate organic acids that more closely mimic root exudates and the by-products of organic matter decomposition, than those typically used to estimate plant available concentrations of trace nutrients (as used in this investigation).

It is suggested that additional pot investigations be conducted to determine optimal fertiliser application rates, as well as to permit the testing of some other key species common to the mine area. Field-testing of some larger herbaceous and woody species should also be considered.

### **10.3 Land disposal of manganese-rich processing wastes**

As direct revegetation of both the SS and EW was not considered viable, land disposal was investigated as a means of disposing of the waste in an environmentally sound manner. Under laboratory conditions it was found that the high application rates tested tended to result in a 'plateau effect' (Basta *et al.*, 2005; see Section 5.2), where, at the very high application rates the soils developed waste-like properties. The exact application rate at which this became evident in the different soils varied depending on soil properties, the parameter selected for comparison and the type of waste.



### 10.3.1 Effect of slag

The most notable effects of applying SS to the soils were a marked increase in soil pH and a reduction in exchangeable acidity. The SS had a high acid-neutralising capacity due to the dissolution of the silicates that consume  $H^+$  ions. An unfortunate consequence of the dissolution of the SS was the release of some heavy metals, notably Mn. Laboratory investigations also indicated that this Mn was not readily soluble or available, but that it was released under acid conditions. Incubation investigation showed that higher amounts of Mn were released in acidic soils than in the more alkaline soils. It is likely that under the alkaline conditions induced by the SS and the aerobic conditions in the soil the Mn would precipitate as insoluble hydroxy species. This occurred quickly in the soils with an initially high pH (e.g. Va). In the acidic soils (e.g. Ia) that had high exchangeable acidity and the potential for continued acid generation (due to organic matter decomposition), concentrations of Mn remained high for a longer period of time. It is also noted that in the more acidic soils, even at the low SS application rates, there was a high release of Mn, probably due to higher concentrations of  $H^+$  ions relative to SS in the soil. It was, however, considered that the laboratory analyses were likely to overestimate the risk of applying the SS to soil. This was, however, refuted by the subsequent pot experiment.

The concentrations of Mn in ryegrass grown in soils treated with SS especially at low application rates, were high relative to the normal ranges reported for ryegrass. This supported the above argument that at the low application rates there was greater dissolution of the SS due to relatively higher concentrations of  $H^+$ . At the high application rates, the SS resulted in elevated soil pH and reduced plant growth, the former reducing the rate of SS dissolution (and release of Mn). It is important to note that typical visual symptoms of Mn toxicity were not evident in any of the plants. It was probable that both Ca and Si ameliorated the toxic effects of high Mn in the plants. The low yield of ryegrass at high application rates and high concentrations of Mn in the foliage at the lower SS application rates suggest that only very low application rates of SS (lower than tested here) can be applied to soil. The current recommendation is not to apply the SS to land until further research has been conducted.

This investigation used SS milled to  $< 2$  mm. It was also indicated that the dissolution of silicates is, at least initially, controlled by amount of acidity and surface area. If this holds

true larger SS aggregates may be less reactive in the soil, especially once a leached layer (where linking cations in the silica tetrahedra have been removed) is formed on the aggregate surface. This may sufficiently reduce the rate at which Mn is released into the soil, allowing both soil and plant processes to negate the potential negative impact. Use of coarser aggregates may also reduce the costs associated with size reduction (milling). The liming potential of the SS could also be considered further, perhaps with an emphasis on use with non-consumable crops (e.g. forestry) or to alleviate acid mine drainage (where solubilised Mn can possibly be recovered by other means, such as electrolysis). A number of avenues for further research are proposed. These are summarised as follows:

1. It has been suggested that the SS may have potential as a liming agent. It is likely that the application rates of SS for purposes of liming will be considerably lower than used in this study. For instance, assuming a lime (with a CCE of 100%) application rate of  $5 \text{ Mg ha}^{-1}$ , an equivalent SS application rate would be about  $12.5 \text{ Mg ha}^{-1}$  (based on a CCE of about 40%). Studies investigating the potential of the SS as a liming agent and the likely risks associated with this (in terms of Mn release from the SS) are required to determine if this is feasible option.
2. Following on from the above proposal, it is necessary to investigate the effect of SS particle size on the dissolution rate of the SS in the soil environment. Consideration should also be given to the long-term impacts of dissolution of larger SS aggregates in a soil environment.

### 10.3.2 Effect of electro-winning waste

Unlike the SS, the most notable consequence of adding EW to the soils was a marked increase in the EC of the soils, driven by the high salinity of the EW. Application rates of EW above  $40 \text{ g kg}^{-1}$  generally resulted in soil EC values above  $200 \text{ mS m}^{-1}$ . This was predicted to result in stunted plant growth, and this was subsequently confirmed in the pot experiment. In addition to the high salinity, the EW also had high amounts of soluble Mn, Ca,  $\text{NH}_4^+$  and  $\text{SO}_4^-$ . The high  $\text{NH}_4^+$  content tended to promote acidification through nitrification processes that encouraged the release of Mn. It was an unexpected finding that, especially at the high EW application rates, the presence of organic matter in the soil promoted the release of Mn from the EW. This effect was not as marked at the lower

application rates. However, the high EC caused by high EW application rates, eliminates the potential for disposal to land at the high rates.

While plant growth was inhibited at the high application rates, there were improvements in yield at application rates of  $< 40 \text{ g kg}^{-1}$ . This was attributed primarily to higher N availability, but probably also other nutrients and trace elements necessary for plant growth. As with the SS, the metal of primary concern was Mn. Elevated tissue concentrations were found in ryegrass grown in soil treated with EW. Additional investigations attempted to reduce Mn uptake by the plants. The potential ameliorating effects of organic matter and lime were investigated, but only resulted in marginal decreases in Mn uptake by ryegrass. However, the P-fertiliser used in one of the pot experiments resulted in a marked reduction in Mn uptake, probably due to the formation of insoluble Mn-P compounds.

The recommendation at this time is not to land apply the EW at the rates tested here. While the leaching column experiment showed that Mn leaching was not likely to be of concern (at the lowest EW application rate) and that the waste has potential as a fertiliser at very low rates, a clearer understanding of some of the mechanisms involved in releasing Mn from the waste is needed. The laboratory and pot experiments suggest that high amounts of Mn can potentially be released, thus a cautious approach is recommended. Once the specific mechanisms of Mn release have been clarified and suitable ameliorative strategies tested, further testing under field conditions may be considered. A number of additional investigations are proposed. The first two proposals are of academic interest, while the last three have more practical applications. These are as follows:

1. A more detailed investigation to consider the effects of organic matter (from soil) on the mobilization of Mn from the waste. The exact mechanism was not elucidated in this study, and it appears that the type and quantity of organic acid in the soil may influence the rate and extent of the dissolution of Mn from the waste.
2. Investigations to determine the relationship between other specific soil properties, notably clay mineralogy and cation and anion exchange capacity, and the behaviour of the EW in the soil.

3. Since addition of P-fertiliser can reduce the amounts of available Mn in soil treated with EW (and also the SS), additional investigations should test the feasibility of using P amendments to reduce Mn availability in the waste. This could be tested in conjunction with other amendments.
4. Given that high Mn uptake by plants is likely when they are grown in soil treated with EW, it is essential that a wider variety of crops be tested, especially those that may be used as forage or food crops.
5. The waste was found to consist of a soluble component, containing high amounts of certain plant nutrients. Leaching of the soluble phase from the EW can be considered as a treatment to clean the waste. The potential of the leachate as a fertiliser can then be tested and the remaining solid waste investigated for potential reprocessing to extract metals (notably Mn and Fe).

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## APPENDICES

### **Appendix 4.1**      Method used for particle size analysis (adapted from Gee and Bauder, 1986)

Air-dry ( $< 2$  mm) material was dispersed by the addition of 10 mL Calgon (35.7 g sodium hexametaphosphate and 7.9 g sodium carbonate  $L^{-1}$ ) and 20 mL distilled water with subsequent ultrasound treatment (400 watt, Labsonic 2000) for 3 minutes. The dispersed sample was passed through a 0.053 mm sieve into a 1 L sedimentation cylinder and made up to the 1 000 mL mark with distilled water.

The  $> 0.053$  mm fraction (sand) was dried at  $105^{\circ}C$  and the  $< 0.053$  mm fraction in the cylinders was brought into suspension by agitation with a custom-made plunger. The coarse silt (0.02-0.053 mm), fine silt (0.002-0.02 mm) and clay ( $< 0.002$  mm) were determined by sedimentation and pipette sampling after appropriate settling times for each size fraction, according to Stokes Law. The pipetted sample was dried overnight at  $105^{\circ}C$ . Separate sub-samples of all  $< 2$  mm materials were dried at  $105^{\circ}C$  overnight for moisture content determination. All fractions are given as a mass percentage of oven-dry soil, after correcting for the moisture content of air-dry samples.



**Appendix 4.2**

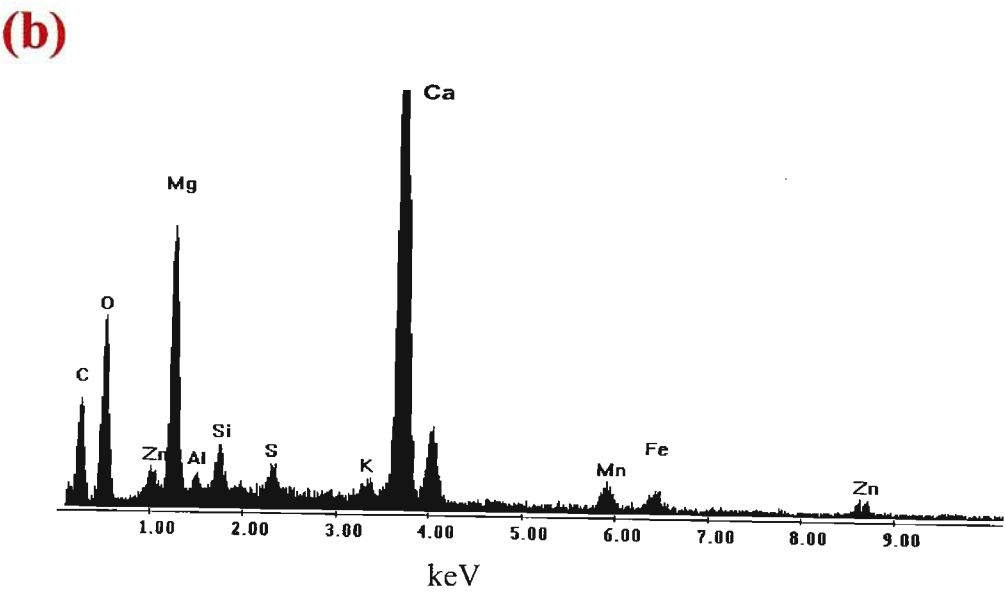
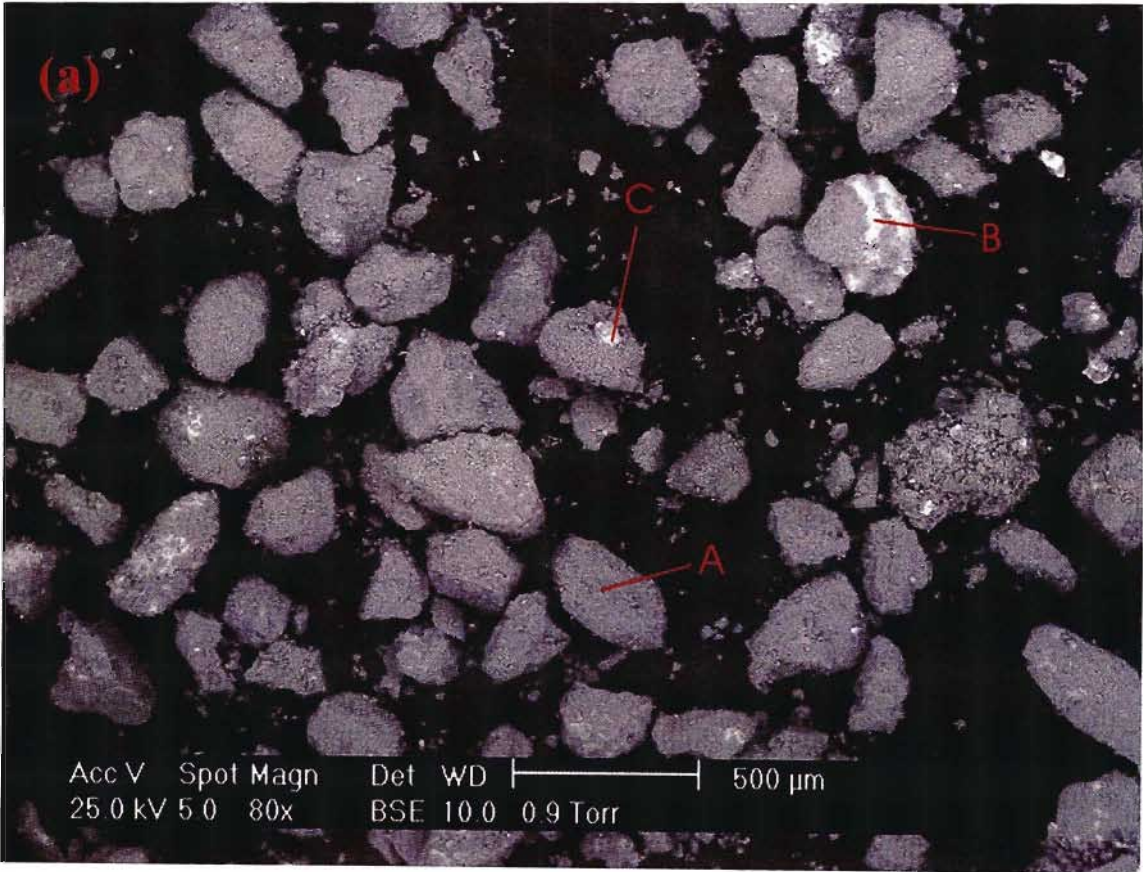
X-ray fluorescence analysis of two samples of tailings from Pering Mine

<b>Major element composition (% oxide)</b>												
<b>Description</b>	<b>SiO<sub>2</sub></b>	<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>Fe<sub>2</sub>O<sub>3</sub></b>	<b>MnO</b>	<b>MgO</b>	<b>CaO</b>	<b>Na<sub>2</sub>O</b>	<b>K<sub>2</sub>O</b>	<b>TiO<sub>2</sub></b>	<b>P<sub>2</sub>O<sub>5</sub></b>	<b>TOTAL</b>	<b>L.O.I.</b>
Sample 1	4.87	1.48	4.03	3.66	32.6	49.9	0.26	0.76	0.05	0.02	97.6	43.0
Sample 2	6.02	1.73	2.73	3.76	32.3	49.6	0.42	0.97	0.12	0.02	97.6	43.0
<b>Minor element composition (mg kg<sup>-1</sup>)</b>												
	<b>S</b>	<b>As</b>	<b>Pb</b>	<b>Zn</b>	<b>Cu</b>	<b>Ni</b>	<b>Cr</b>	<b>V</b>	<b>Ba</b>	<b>Sr</b>	<b>Rb</b>	
Sample 1	18564	85	311	2170	6.2	4.4	2.8	5.5	0.8	17.2	8.0	
Sample 2	15400	109	398	5481	22.6	0.1	3.6	11.8	11.5	15.0	8.8	
<b>Minor element composition (mg kg<sup>-1</sup>)</b>												
	<b>Th</b>	<b>Y</b>	<b>Zr</b>	<b>Sc</b>	<b>Ga</b>	<b>Ce</b>	<b>U</b>	<b>Nd</b>	<b>Sn</b>	<b>La</b>	<b>Nb</b>	
Sample 1	3.9	0.8	5.3	0.3	2	3	bd	bd	bd	bd	bd	
Sample 2	6.5	2.2	7.2	0.5	5	bd	bd	bd	bd	bd	bd	

L.O.I. Loss on ignition at about 1000°C.

bd below detection.

**Appendix 4.3** (a) Scanning electron microscope image and (b) typical EDX trace of tailings from Pering Mine. The general dolomitic matrix (A) consists predominantly of Ca and Mg with minor amounts of Zn, S, Si, Fe and Al. The white bands (B) had high amounts of Zn and S (sphalerite), while some of the bright spots (C) had elevated levels of Fe and S (pyrite)



#### Appendix 4.4 Brief description of grass species tested in Pb/Zn tailings material (adapted from Gibbs Russell *et al.* (1990) and van Oudtshoorn (2002))

##### *Andropogon eucomus*

Snowflake grass is a perennial tufted species with red culms, producing conspicuously fluffy white inflorescences. It grows well in wet areas such as vleis, riverbanks and seepage areas, especially in disturbed sandy soils. It is often an indicator of poorly drained soils. It is a sub-climax grass species falling in to the increaser II<sup>3</sup> category.

##### *Cenchrus ciliaris*

Fox-tail or blue buffalo grass is a perennial tufted grass with a shrub-like growth form. It produces dense straw-coloured inflorescences. It is widespread, but prefers the dry, warm parts of South Africa. It grows in almost all soils but mostly in sandy or well-drained soils. It is difficult to establish in clay soils, but once established grows well. It is a palatable species, often planted as a pasture grass. It is classed as a sub-climax to climax, decreaser species.

##### *Cymbopogon plurinodis*

Narrowed-leaved turpentine grass is a persistent, dense, tufted perennial species that grows in open grassland. It grows in all soils but prefers heavier soil types. This is a highly unpalatable species due to bitter, turpentine-smelling essential oils in the plant. It is classed as both an increaser I and increaser III, climax grass species.

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<sup>3</sup> Grasses are generally classified according to their ecological status as a response to different levels of grazing (van Oudtshoorn, 2002). These are decreaser and increaser I, II, and III.

- Decreaser species are abundant in good quality veld, but decrease in frequency when the veld is over or undergrazed. These grasses are typically sought-after palatable climax grass species.
- Increaser I species tend to be common in underutilized veld, and are generally unpalatable robust species that grow well with little defoliation.
- Increaser II species tend to be abundant in overgrazed veld. They are also typically unpalatable pioneer and sub-climax species that have not been heavily grazed and as such out-compete more palatable species that have been weakened by grazing.
- Increaser III species are also unpalatable species that dominate in overgrazed veld. These species, however, tend to be climax species that are very difficult to remove once established.

Some grasses may not conform to the above categories, as widespread distributions of some species lead to ecotype variations that create differences in growth response. It should be noted that some grasses are classified as exotic or invaders, typically being pioneer and sub-climax species.

*Digitaria eriantha*

Common fingergrass is a widespread, highly palatable, perennial grass species, with commercial varieties being used in cultivated pastures (e.g. Smuts fingergrass). It is a persistent perennial species that produce stolons. It grows well in sandy and gravelly soils in the more arid parts of South Africa and also in damp soils near vleis. It is considered a climax species of the decreaser class.

*Eragrostis superba*

Saw-tooth love grass is a weak, tufted, perennial grass, with reasonably hard culms that can form dense tufts. It is common in disturbed sites, such as roadsides or bare patches. It prefers loamy, sandy or gravelly soils but will also grow in clay soils. It is highly palatable during early growth, but less so when mature. It grows quickly and is used as a drought resistant pasture in some countries. It is also sometimes used to revegetate bare patches in veld. It is a sub-climax, increaser II species.

*Eragrostis tef*

Tef is an exotic annual species, originally developed as a pasture and hay grass. It grows fast and establishes easily, and as such is often used to revegetate bare ground. It has gained some favour in mine reclamation work as a 'nurse crop', prior to establishing more persistent, slower growing perennial species.

*Fingeruthia africana*

Thimble grass is a tufted perennial usually found growing in gravelly soil, often in limestone and eroded places. It is not a common veld grass offering only moderate palatability. It is a sub-climax to climax grass species, and plays an important role stabilising soil in eroded areas. It is a decreaser species.

**Appendix 4.5** Nitric acid wet digestion method (adapted from Slatter, 1998)

Between 0.5 and 1 gram of plant material was weighed into 75 mm digestion tubes (with reflux lids) and 10 mL concentrated nitric acid was added. Plant material was allowed to predigest overnight at room temperature. The tubes were placed in a digestion block and digested for about five hours at a temperature between 127 and 130 °C. The digestion was considered complete when there were no more visible signs of plant material in the digestion tube and the liquid was clear. Once the digestion was complete, the tubes were left to cool and then the contents of each tube were filtered into 50 mL volumetric flasks. The digestion tubes were then rinsed with distilled water to remove residual digest into the same flasks. The digests were made up to volume with distilled water and decanted into 100 mL plastic vials. These were stored at 4 °C for further analysis.

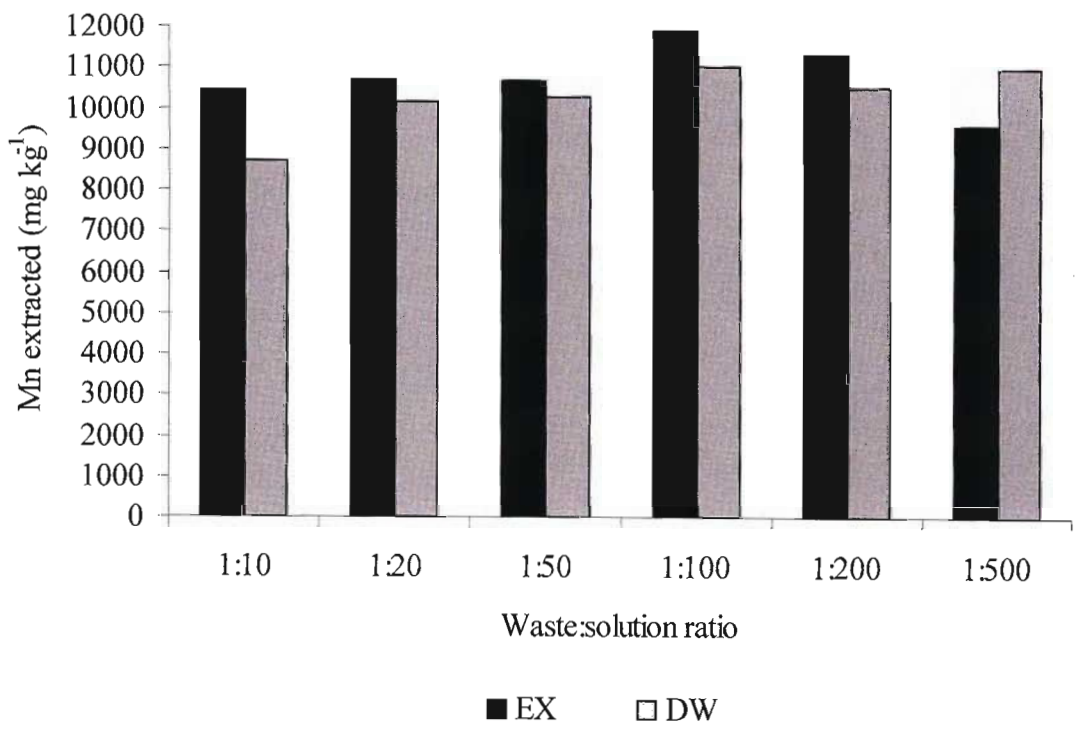
**Appendix 6.1** X-ray fluorescence analysis of slag (SS) from the Samancor Mn-smelter and electro-winning waste (EW) from MMC

Major element composition (% oxide)												
Description	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	TOTAL	L.O.I.
SS	37.4	4.83	0.79	19.4	7.61	26.2	0.13	0.16	0.19	0.01	96.4	0.00
EW	5.26	1.11	37.9	30.2	0.57	5.77	bd	bd	0.05	0.14	79.3	17.7
Minor element composition (mg kg <sup>-1</sup> )												
	S	As	Pb	Zn	Cu	Ni	Cr	V	Ba	Sr	Rb	
SS	14499	bd	2.0	bd	bd	bd	bd	8.4	2283	835	8.7	
EW	207956	119	839	274	265	39.3	bd	63.0	8221	4446	10.9	
Minor element composition (mg kg <sup>-1</sup> )												
	Th	Y	Zr	Sc	Ga	Ce	U	Nd	Sn	La	Nb	
SS	12.6	39.7	96.9	0.2	3.0	11.0	11.6	1.00	bd	bd	1.6	
EW	17.8	35.8	2.4	2.3	8.0	bd	9.8	bd	bd	3.4	bd	

L.O.I. Loss on ignition.

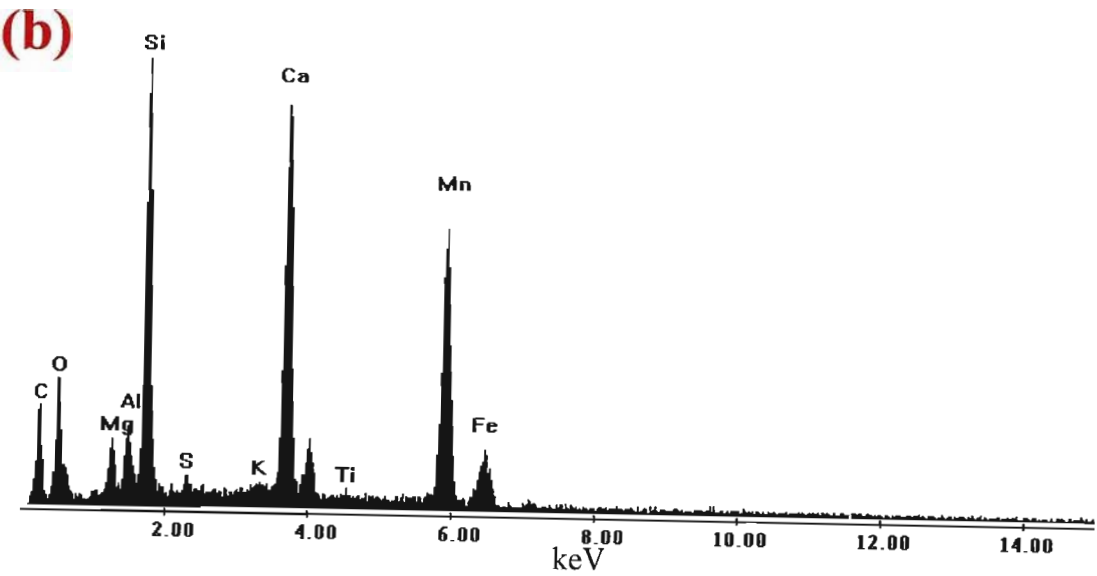
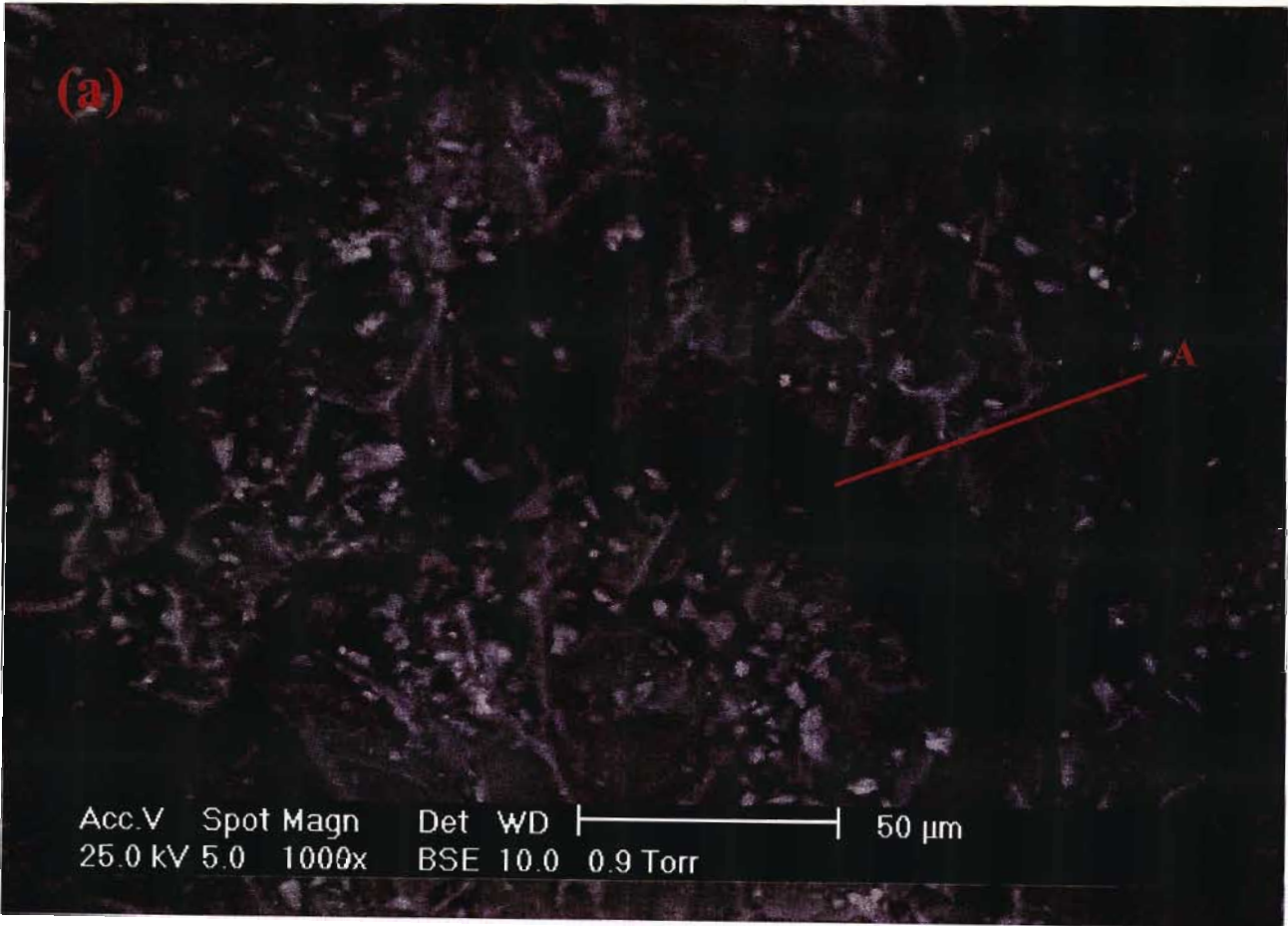
bd below detection.

**Appendix 6.2**      Comparison of Mn concentrations in electro-winning waste from MMC extracted with either 0.05 M CaCl<sub>2</sub> (exchangeable - EX) or distilled water (DW) at different waste:solution ratios



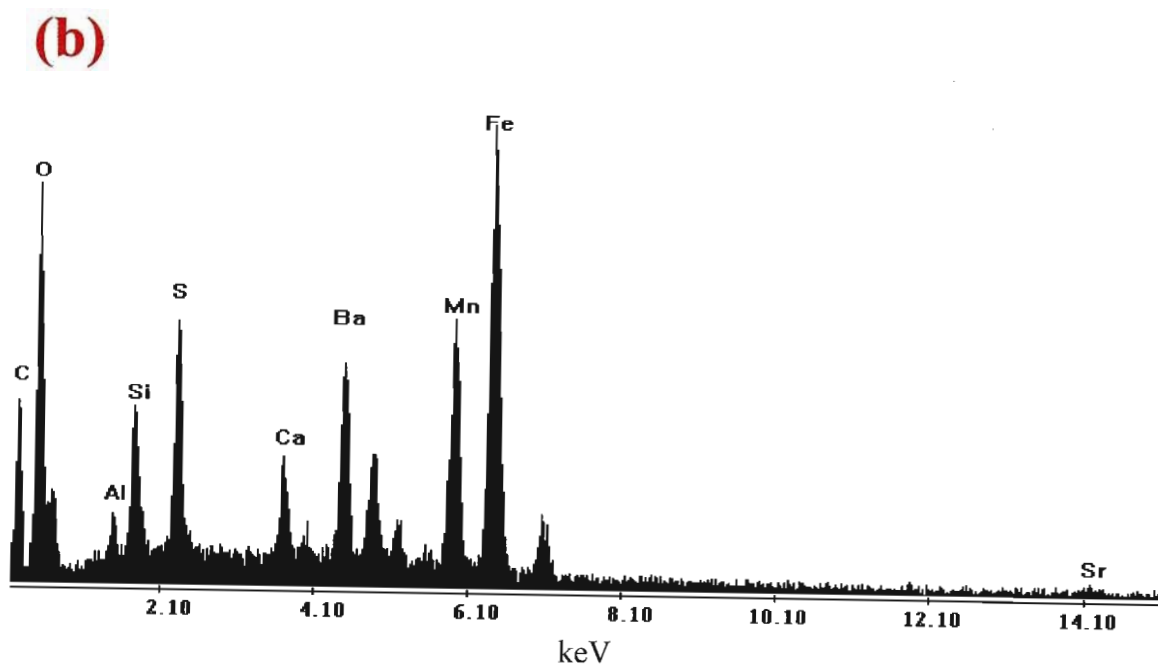
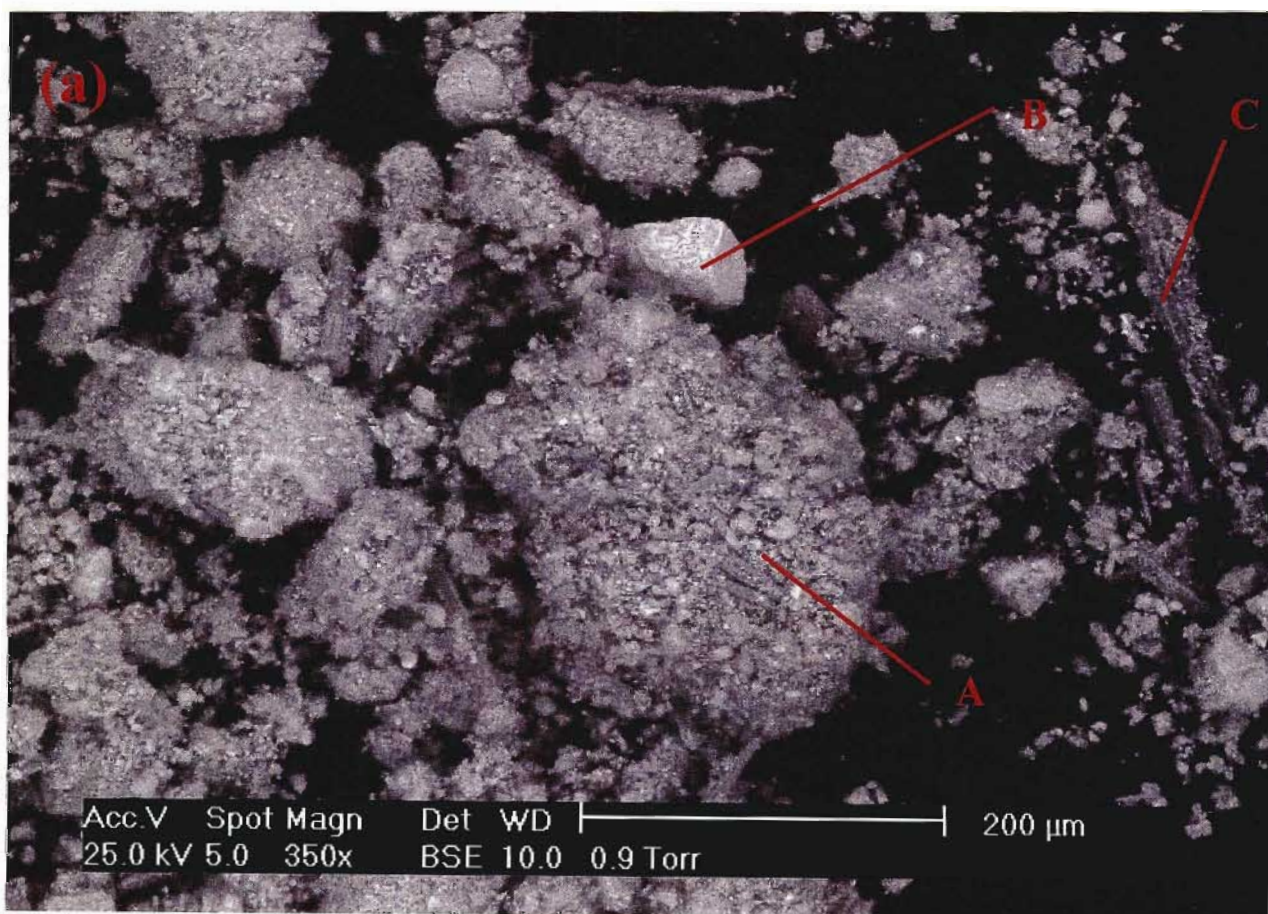
Appendix 6.3

(a) Scanning electron microscope image and (b) a typical EDX trace of a crushed slag particle from the Samancor Mn-smelter. The dark patch (A) was identified as carbon, while the lighter surrounding areas consisted mainly of Si, Ca, and Mn (constituting the mineral glaucochroite), with some other trace constituents (Fe, Al, Mg, S and Ti)





**Appendix 6.4** (a) Scanning electron microscope image and (b) a typical EDX trace of MMC electro-winning waste. The area labelled (A) consisted primarily of Mn, Fe, Ca, S, and variable amounts of Si, Ba and Sr. The granule labelled (B) consisted predominantly of S, Ba and Sr (indicating the presence of barite). The lath-like crystals (C) were predominantly Ca and S indicating the presence of gypsum



**Appendix 6.5** Light-microscope images of the crushed (< 2 mm) slag from the Samancor Mn-smelter showing the glassy and pitted nature of some of the fragments



# Appendix 8.1

Final pH and concentrations of 0.05 M CaCl<sub>2</sub>-extractable metals in incubated Bonheim (Bo), Hutton, (Hu), Inanda (Ia), Longlands (Lo), Shortlands (Sd) and Valsrivier (Va) soil after the addition of slag from the Samancor Mn-smelter at rates of 0, 30, 60, 120, 240 and 480 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	pH						Mn						Fe						Co					
		Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va
0	0	6.0	4.1	3.9	4.8	6.3	6.5	149	120	10.0	31.8	122	25.5	8.7	3.7	9.6	1.7	3.3	bd	1.3	1.8	0.8	4.3	3.2	bd
30		7.0	4.2	4.6	6.7	6.9	7.1	344	342	412	128	165	101	6.6	12.8	4.4	4.0	4.5	bd	0.8	bd	bd	8.2	5.0	1.0
60		7.0	4.7	4.9	7.1	7.2	7.2	387	350	504	150	196	81.6	4.7	10.4	4.7	2.5	5.3	bd	0.5	bd	bd	8.0	5.4	2.1
120		7.4	7.0	6.3	7.0	7.8	7.3	412	451	1224	134	240	95.7	4.3	12.9	5.8	3.5	5.2	bd	0.5	bd	bd	8.6	4.8	2.4
240		7.2	7.2	6.9	7.2	7.8	7.4	428	368	1112	112	240	85.1	6.2	10.2	6.0	3.1	5.5	bd	0.3	bd	bd	8.2	5.9	2.3
480		7.1	7.2	7.4	7.7	7.5	8.0	395	305	724	81.0	116	52.7	5.3	9.5	5.0	3.2	5.3	bd	0.1	bd	bd	8.6	6.2	2.4
0	3	6.3	4.4	4.0	5.0	6.3	6.5	161	216	35.5	50.1	154	67.1	4.1	2.3	16.8	bd	5.1	bd	bd	2.9	2.5	6.4	5.9	3.1
30		7.1	4.3	4.8	6.7	7.2	7.2	308	328	617	129	139	65.5	5.8	11.0	6.1	4.4	4.7	bd	0.5	bd	bd	8.3	4.9	2.1
60		7.2	5.0	5.2	6.9	7.5	7.3	249	367	820	117	135	56.8	3.6	11.9	7.2	bd	bd	bd	0.6	bd	bd	bd	0.4	bd
120		7.5	7.1	6.4	7.0	7.8	7.3	268	418	1222	108	157	56.4	4.5	11.6	4.8	bd	bd	bd	1.1	bd	bd	bd	bd	bd
240		7.4	7.2	6.8	7.0	7.8	7.4	259	540	1426	89.9	187	45.0	3.0	10.3	7.1	bd	bd	bd	2.4	bd	bd	bd	1.6	1.0
480		7.4	7.2	7.3	7.8	7.7	8.0	282	281	936	38.8	160	18.6	4.5	11.8	7.9	bd	bd	bd	0.8	bd	bd	bd	bd	1.8
0	7	6.2	4.1	3.9	5.0	6.4	6.5	239	241	22.4	51.3	191	80.9	4.4	2.7	19.2	1.6	5.5	bd	bd	2.5	3.6	9.7	8.7	3.4
30		7.1	4.4	4.7	6.8	7.5	7.2	331	288	646	126	156	18.1	3.7	13.1	6.4	bd	bd	bd	1.0	bd	bd	1.4	bd	1.3
60		7.3	5.9	5.3	6.9	7.7	7.3	203	352	1045	114	110	23.5	5.0	11.9	7.2	bd	bd	bd	1.1	bd	bd	1.5	1.1	1.9
120		7.5	7.1	6.5	7.0	7.8	7.4	193	366	1466	107	119	44.9	4.0	10.4	8.0	bd	bd	bd	0.8	bd	bd	1.3	1.2	1.1
240		7.5	7.2	7.0	7.1	7.9	7.3	189	332	1192	93.2	156	41.6	4.4	11.0	7.0	bd	bd	bd	0.7	bd	bd	1.6	3.2	1.2
480		7.5	7.2	7.3	7.8	7.8	7.9	359	302	936	41.4	180.1	bd	4.9	10.7	5.4	bd	bd	bd	1.3	bd	bd	2.1	0.9	1.0
0	14	6.1	4.3	4.0	5.1	6.3	6.5	345	395	7.6	43.4	123	37.5	6.2	3.7	20.2	1.0	6.7	bd	1.6	3.8	3.3	11.4	11.1	5.6
30		7.0	6.3	4.9	6.8	7.4	7.1	120	113	838	105	84.3	bd	5.1	10.2	7.8	bd	bd	bd	1.0	bd	bd	1.8	2.0	1.7
60		7.4	6.1	5.4	7.0	7.8	7.0	97.3	91.7	948	112	59.7	bd	4.9	11.5	6.6	bd	bd	bd	1.9	bd	bd	2.3	2.3	1.7
120		7.3	7.0	6.7	6.8	7.9	7.2	111	211	1379	96.9	64.2	bd	6.3	13.9	6.6	bd	bd	bd	2.2	bd	bd	2.0	1.8	2.0
240		7.6	7.2	7.1	7.1	7.9	7.2	116	163	1243	85.6	74.5	21.4	4.5	14.1	7.1	bd	bd	bd	1.3	bd	bd	2.4	0.9	1.4
480		7.6	7.2	7.4	7.7	7.8	7.4	275	208	16241	43.4	103	12.7	5.4	12.8	9.3	bd	bd	bd	1.3	bd	bd	1.9	1.5	2.1

bd below detection.

**Appendix 8.1. (contd.)**

Final pH and concentrations of 0.05 M CaCl<sub>2</sub>-extractable metals in incubated Bonheim (Bo), Hutton, (Hu), Inanda (Ia), Longlands (Lo), Shortlands (Sd) and Valsrivier (Va) soil after the addition of slag from the Samancor Mn-smelter at rates of 0, 30, 60, 120, 240 and 480 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	pH						Mn						Fe						Co					
		Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va
0	28	6.3	4.1	4.0	5.0	6.3	6.5	423	244	18.2	49.8	147	63.7	6.2	2.3	18.3	1.6	7.6	bd	2.3	2.3	4.3	13.3	13.4	bd
30		7.2	5.0	4.9	6.8	7.5	7.2	174	63.1	991	68.0	77.8	bd	4.5	11.8	8.0	bd	bd	bd	2.1	bd	bd	2.3	1.3	1.6
60		7.4	6.9	5.7	7.0	7.8	7.1	146	23.0	1019	104	68.5	bd	6.1	10.3	7.3	bd	bd	bd	1.0	bd	bd	3.8	3.1	3.6
120		7.5	7.2	6.9	7.0	7.8	7.2	124	27.0	1618	93.0	60.4	bd	5.8	11.0	9.0	bd	bd	bd	1.7	1.1	bd	3.3	2.7	3.6
240		7.5	7.3	7.3	7.1	7.9	7.4	131	35.6	1132	93.5	72.7	bd	4.8	11.2	8.5	bd	bd	bd	2.7	1.2	bd	2.7	2.4	2.5
480		7.6	7.1	7.4	7.6	7.8	7.4	328	138	1168	40.0	89.5	9.5	5.5	13.5	9.8	bd	bd	bd	1.6	1.3	bd	2.9	2.9	4.2
0	56	6.2	4.1	4.0	4.8	6.3	6.6	327	198	8.7	40.6	160	60.6	4.2	2.3	13.8	1.8	2.5	bd	1.5	bd	bd	3.2	bd	bd
30		7.1	4.9	5.0	6.9	7.6	7.2	126	61.5	753	39.9	64.5	bd	5.4	12.1	9.5	bd	bd	bd	1.7	bd	bd	3.3	3.0	1.3
60		7.2	6.2	6.0	7.0	7.8	7.2	135	bd	1414	45.5	54.3	bd	7.4	11.7	9.2	bd	bd	bd	1.6	bd	bd	3.1	2.0	2.0
120		7.4	4.1	6.9	7.0	7.8	7.3	133	11.7	1951	80.6	58.2	bd	5.7	11.2	10.6	bd	bd	bd	2.6	bd	bd	3.3	2.8	2.4
240		7.7	7.2	7.5	7.1	7.8	7.4	155	3.3	1108	80.0	63.2	bd	8.0	8.5	7.9	bd	bd	bd	1.6	bd	bd	4.3	2.5	3.9
480		7.5	7.3	7.4	7.2	7.8	7.5	354	19.5	869	43.0	72.3	bd	5.2	7.3	10.0	bd	bd	bd	2.1	bd	bd	3.3	3.1	3.2
0	84	5.6	4.2	4.0	4.8	6.2	6.5	528	115	9.4	29.2	95.3	29.8	4.9	4.2	14.9	7.9	4.0	bd	1.5	2.2	0.6	4.4	1.6	bd
30		7.3	5.2	5.0	7.0	7.6	7.2	147	50.2	509	35.4	67.8	bd	4.6	8.5	9.9	bd	bd	bd	1.0	bd	bd	4.2	2.2	2.9
60		7.4	6.7	6.0	7.1	7.7	7.2	147	2.8	1364	33.9	64.5	bd	6.4	7.3	8.9	bd	bd	bd	2.3	bd	bd	4.4	3.8	3.9
120		7.5	7.1	6.9	7.1	7.8	7.3	154	0.5	1278	57.9	59.5	bd	5.0	7.6	8.3	bd	bd	bd	2.1	bd	bd	4.1	3.7	2.4
240		7.7	7.4	7.3	7.1	7.8	7.4	33.3	2.8	999	51.0	bd	bd	5.0	7.7	6.6	bd	bd	bd	bd	bd	bd	1.2	bd	bd
480		7.6	7.4	7.5	7.3	7.8	7.5	149	13.4	794	17.5	bd	bd	6.8	10.1	5.2	bd	bd	bd	bd	bd	bd	1.2	bd	bd
0	140	5.8	3.9	4.0	4.9	6.2	6.5	328	214	18.5	48.2	106	53.8	4.7	4.2	13.6	4.2	5.3	bd	1.8	bd	2.5	6.5	2.1	2.8
30		7.2	4.4	5.0	6.8	7.6	7.2	46.2	41.6	238	14.3	bd	bd	5.7	8.8	4.9	bd	bd	bd	bd	1.2	bd	1.8	bd	bd
60		7.4	6.6	6.1	7.1	7.6	7.2	32.9	bd	867	12.4	bd	bd	4.0	10.9	5.9	bd	2.3	bd	bd	1.5	bd	1.0	bd	bd
120		7.5	6.8	6.9	7.1	7.4	7.3	43.0	3.1	1154	27.0	bd	bd	6.5	7.6	4.6	bd	4.3	bd	bd	bd	bd	1.1	bd	bd
240		7.7	7.4	7.3	7.2	7.7	7.3	42.3	1.7	843	41.1	bd	bd	3.2	9.1	4.6	1.3	5.0	bd	bd	bd	bd	bd	bd	bd
480		7.6	7.3	7.5	7.2	7.8	7.6	90.7	bd	772	24.9	bd	bd	5.5	6.8	4.1	bd	bd	bd	bd	1.7	bd	1.1	bd	bd

bd below detection.



**Appendix 8.1. (contd.)**

Final pH and concentrations of 0.05 M CaCl<sub>2</sub>-extractable metals in incubated Bonheim (Bo), Hutton, (Hu), Inanda (Ia), Longlands (Lo), Shortlands (Sd) and Valsrivier (Va) soil after the addition of slag from the Samancor Mn-smelter at rates of 0, 30, 60, 120, 240 and 480 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	Cu						Pb						Zn						Ni					
		Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va
0	0	2.2	2.1	bd	bd	bd	bd	6.7	2.7	bd	5.4	4.1	3.8	0.7	4.2	2.3	0.8	bd	2.7	bd	2.9	bd	bd	bd	bd
30		1.5	2.0	bd	2.6	bd	bd	1.6	6.3	1.5	5.7	3.9	5.3	2.0	2.3	bd	0.6	2.1	2.5	bd	bd	bd	bd	bd	bd
60		1.2	0.9	bd	2.7	bd	bd	4.4	3.2	1.2	4.9	8.3	5.3	1.7	3.7	bd	1.7	bd	2.3	bd	bd	bd	bd	bd	bd
120		1.4	bd	bd	2.9	bd	bd	2.0	bd	bd	3.8	5.7	5.5	bd	3.5	bd	1.0	1.0	2.4	bd	3.0	bd	bd	bd	bd
240		1.4	bd	bd	2.7	bd	bd	bd	2.7	1.4	5.8	3.7	6.3	bd	2.2	bd	1.0	1.2	7.3	bd	bd	bd	bd	bd	bd
480		2.3	bd	bd	2.6	bd	bd	3.2	3.7	1.1	6.0	7.9	5.4	0.1	2.7	bd	1.5	1.2	6.8	bd	bd	bd	bd	bd	bd
0	3	bd	bd	bd	bd	bd	bd	6.1	4.9	bd	3.7	2.5	bd	0.6	1.8	2.0	0.9	1.3	2.1	bd	0.4	1.7	bd	bd	bd
30		2.5	bd	bd	3.0	bd	bd	1.4	3.6	bd	5.0	5.9	6.3	0.7	1.3	bd	2.3	1.2	2.8	bd	bd	bd	bd	bd	bd
60		bd	bd	bd	bd	bd	bd	3.4	3.9	2.4	2.5	bd	bd	0.3	3.0	bd	3.0	1.1	bd	bd	bd	bd	bd	bd	bd
120		bd	bd	bd	bd	bd	bd	bd	4.8	bd	2.4	2.8	2.9	0.2	1.3	bd	2.7	bd	bd	bd	bd	bd	bd	bd	bd
240		bd	bd	bd	bd	bd	bd	bd	3.3	bd	2.8	bd	bd	bd	2.0	bd	5.2	bd	bd	bd	bd	bd	bd	bd	2.7
480		1.0	1.1	bd	bd	bd	bd	bd	6.5	1.2	2.5	bd	bd	0.7	2.0	bd	3.3	bd	bd	bd	2.1	bd	bd	bd	3.0
0	7	bd	bd	bd	bd	bd	bd	6.4	bd	1.2	6.4	6.0	3.8	0.5	3.1	1.4	2.7	bd	1.6	1.7	bd	1.5	bd	bd	bd
30		bd	bd	bd	bd	bd	bd	1.3	5.4	bd	1.8	bd	bd	bd	1.5	bd	4.4	bd	bd	bd	1.4	bd	bd	bd	3.4
60		bd	bd	bd	bd	bd	bd	0.5	6.5	bd	2.9	2.8	bd	bd	3.3	bd	3.5	bd	bd	bd	bd	bd	bd	bd	bd
120		bd	bd	bd	bd	bd	bd	bd	4.5	bd	3.1	2.1	bd	bd	2.2	bd	4.4	bd	bd	bd	bd	bd	bd	bd	bd
240		bd	bd	bd	bd	bd	bd	bd	4.6	3.2	3.1	bd	bd	bd	0.7	bd	4.7	2.1	bd	bd	1.6	bd	bd	bd	3.1
480		bd	bd	bd	bd	bd	bd	bd	6.4	1.3	2.3	bd	bd	bd	1.7	bd	4.3	bd	1.1	bd	bd	bd	bd	bd	5.6
0	14	bd	1.4	bd	bd	bd	bd	3.8	4.0	1.2	7.3	4.1	4.6	0.8	4.7	2.3	2.5	bd	2.5	1.8	3.3	1.7	2.5	2.9	bd
30		bd	bd	bd	bd	bd	bd	bd	5.2	2.9	4.4	bd	3.0	bd	2.0	bd	2.9	bd	1.3	bd	2.4	bd	bd	bd	3.4
60		bd	bd	bd	bd	bd	bd	bd	5.7	bd	5.3	2.2	bd	3.5	1.5	bd	4.0	1.2	1.2	bd	bd	bd	bd	bd	3.9
120		bd	bd	bd	bd	bd	bd	1.6	3.1	1.3	5.7	bd	bd	bd	1.0	bd	5.2	1.3	1.2	bd	bd	bd	bd	bd	4.4
240		bd	1.1	bd	bd	bd	bd	bd	6.4	1.9	5.0	2.4	bd	1.3	1.1	bd	3.2	bd	2.4	bd	bd	bd	bd	bd	6.1
480		bd	bd	bd	bd	bd	bd	bd	6.6	3.3	4.9	bd	2.5	0.7	2.6	bd	4.0	1.1	1.8	bd	bd	bd	bd	bd	5.5

bd below detection.

**Appendix 8.1. (contd.)** Final pH and concentrations of 0.05 M CaCl<sub>2</sub>-extractable metals in incubated Bonheim (Bo), Hutton, (Hu), Inanda (Ia), Longlands (Lo), Shortlands (Sd) and Valsrivier (Va) soil after the addition of slag from the Samancor Mn-smelter at rates of 0, 30, 60, 120, 240 and 480 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	Cu						Pb						Zn						Ni					
		Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va
0	28	bd	bd	bd	bd	bd	bd	4.0	bd	bd	7.7	4.2	4.2	0.7	2.8	1.6	3.7	bd	1.9	bd	bd	1.8	2.2	2.0	2.8
30		bd	bd	bd	bd	bd	bd	bd	7.8	bd	7.4	bd	2.3	0.4	0.7	bd	4.2	bd	1.8	bd	2.5	bd	bd	bd	4.7
60		bd	bd	bd	bd	bd	bd	bd	5.6	4.0	4.8	bd	2.2	bd	1.4	bd	3.3	1.0	1.8	bd	bd	bd	bd	bd	4.6
120		bd	bd	bd	bd	bd	bd	1.8	5.7	1.9	5.3	2.1	bd	2.0	3.8	bd	3.2	1.1	2.1	bd	bd	bd	bd	bd	5.2
240		bd	bd	bd	bd	bd	bd	1.6	6.3	2.4	7.6	bd	bd	3.5	1.6	bd	3.2	bd	2.3	bd	bd	bd	bd	bd	5.7
480		bd	bd	bd	bd	bd	bd	4.0	7.0	2.8	7.9	bd	bd	bd	3.1	bd	3.0	1.2	3.0	bd	2.7	bd	bd	2.0	6.3
0	56	bd	0.7	bd	1.3	bd	bd	2.7	2.4	bd	2.4	2.1	bd	bd	2.1	1.3	1.4	1.9	4.7	bd	bd	bd	bd	bd	bd
30		bd	bd	bd	bd	bd	bd	1.1	6.9	2.6	8.0	3.4	3.4	bd	4.4	bd	3.3	bd	2.8	bd	bd	bd	bd	bd	8.2
60		bd	bd	bd	bd	bd	bd	2.7	5.4	1.6	10.0	bd	2.0	bd	1.6	bd	4.2	bd	4.3	bd	bd	bd	bd	bd	7.0
120		bd	3.2	bd	bd	bd	bd	1.0	4.6	2.8	7.6	3.9	bd	bd	4.6	bd	3.7	bd	3.0	bd	bd	bd	bd	bd	8.0
240		bd	1.9	bd	bd	bd	bd	2.5	2.3	3.7	8.4	3.5	bd	bd	0.6	bd	3.8	bd	3.5	bd	bd	bd	bd	bd	7.6
480		bd	1.4	bd	bd	bd	bd	3.2	2.7	3.0	8.0	5.0	bd	1.1	0.5	bd	3.2	1.1	3.2	bd	bd	bd	bd	2.7	7.1
0	84	bd	2.1	bd	2.4	bd	bd	bd	3.6	3.1	1.8	1.6	bd	1.0	4.5	2.5	1.6	1.1	2.5	2.2	bd	2.0	bd	bd	bd
30		bd	1.5	bd	bd	bd	bd	1.7	3.6	5.0	8.5	2.4	bd	0.2	0.9	bd	3.7	bd	3.3	bd	bd	bd	bd	bd	7.4
60		bd	1.2	bd	bd	bd	bd	bd	bd	3.4	8.1	bd	bd	bd	1.9	bd	6.0	1.2	4.6	bd	bd	bd	bd	bd	8.0
120		bd	1.4	bd	bd	bd	bd	bd	bd	3.4	8.1	2.7	bd	bd	2.1	bd	3.9	1.4	3.7	bd	bd	bd	bd	bd	9.2
240		1.3	2.4	bd	bd	bd	bd	bd	bd	bd	5.0	bd	bd	0.2	4.1	bd	3.9	bd	3.7	bd	bd	bd	bd	bd	1.1
480		1.0	1.8	bd	bd	bd	bd	2.3	2.7	bd	1.4	bd	bd	0.2	0.4	bd	4.0	bd	3.8	bd	bd	bd	bd	bd	2.7
0	140	bd	0.6	bd	2.3	bd	bd	3.7	bd	2.4	3.6	5.9	3.3	0.3	2.5	1.5	1.4	2.0	2.5	bd	bd	bd	bd	bd	bd
30		bd	1.6	bd	bd	bd	bd	bd	bd	bd	3.0	bd	bd	bd	0.3	bd	4.1	bd	3.9	bd	bd	bd	bd	bd	1.2
60		bd	1.7	bd	bd	bd	bd	bd	2.8	bd	2.5	bd	bd	0.2	bd	bd	4.5	bd	4.1	bd	bd	bd	bd	bd	2.2
120		1.1	0.9	bd	bd	bd	bd	bd	2.9	bd	3.0	bd	bd	0.4	0.5	bd	3.8	bd	5.3	bd	bd	bd	2.2	bd	2.3
240		bd	1.3	bd	bd	bd	bd	bd	2.2	bd	3.3	bd	bd	0.5	1.1	bd	4.3	bd	4.3	bd	bd	bd	bd	bd	2.7
480		bd	1.6	bd	bd	bd	bd	bd	5.6	bd	3.8	bd	bd	0.6	3.0	bd	4.3	1.0	4.6	bd	bd	bd	bd	bd	3.1

bd below detection.

**Appendix 8.2.** Final pH and concentrations of 0.05 M CaCl<sub>2</sub>-extractable metals in incubated Bonheim (Bo), Hutton, (Hu), Inanda (Ia), Longlands (Lo), Shortlands (Sd) and Valsrivier (Va) soil after the addition of electro-winning waste at rates of 0, 20, 40, 80, 160 and 320 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	pH						Mn						Fe						Co					
		Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va
0	0	6.0	4.1	3.9	4.8	6.3	6.5	149	120	10.0	31.8	1226	25.5	8.7	3.7	9.6	1.7	3.3	bd	1.3	1.8	0.8	4.3	3.2	bd
20		6.1	4.6	4.1	5.4	6.4	6.5	477	488	650	204	226	396	4.9	3.2	7.3	bd	3.7	bd	1.1	2.3	3.9	4.3	2.7	1.4
40		6.1	4.4	4.3	5.7	6.4	6.6	440	741	1050	486	603	497	2.4	4.3	8.1	bd	4.2	bd	1.8	2.9	4.2	6.5	5.1	2.5
80		6.0	4.3	4.5	6.0	6.7	6.7	1208	1518	2103	1067	999	982	3.6	3.3	9.2	0.9	3.3	bd	4.6	6.5	10.5	11.5	7.4	4.4
160		6.1	4.3	4.8	6.2	6.6	6.7	1855	2335	4790	1816	1882	2012	2.8	3.0	7.9	bd	3.9	bd	6.8	13.6	19.4	15.0	9.6	1bd
320		6.6	4.5	5.2	6.3	6.6	6.4	4662	4998	6355	3130	4059	4645	4.0	3.8	7.1	bd	3.5	bd	14.9	25.6	30.3	18.1	17.9	22.8
0	3	6.3	4.4	4.0	5.0	6.3	6.5	161	216	35.5	50.1	154	67.1	4.1	2.3	16.8	bd	5.1	bd	bd	2.9	2.5	6.4	5.9	3.1
20		6.2	4.8	4.2	5.5	5.6	6.6	330	517	584	313	420	279	4.5	3.2	12.3	0.9	5.0	bd	bd	4.4	4.7	7.6	7.9	3.2
40		6.1	4.5	4.3	5.7	5.0	6.5	724	912	1052	838	688	545	3.3	2.5	11.0	2.9	6.0	bd	1.4	6.0	6.7	12.2	7.9	5.8
80		5.7	4.6	4.4	6.0	6.5	6.5	1315	1356	1782	1275	1232	1097	5.5	2.8	11.4	3.2	4.9	bd	3.3	10.7	9.5	13.7	10.4	6.5
160		6.4	4.4	4.7	6.1	7.0	6.4	1795	2648	3937	2045	1865	2397	3.0	3.1	11.8	0.6	5.4	bd	5.8	12.0	18.0	17.0	13.2	12.8
320		6.6	4.7	5.2	6.2	6.8	6.4	3327	5075	4853	3423	4566	5153	3.3	2.9	9.1	0.8	5.5	bd	10.7	21.1	26.8	23.3	18.9	25.8
0	7	6.2	4.1	3.9	5.0	6.4	6.5	239	241	22.4	51.3	191	80.9	4.4	2.7	19.2	1.6	5.5	bd	bd	2.5	3.6	9.7	8.7	3.4
20		5.8	4.1	4.8	5.6	6.1	6.5	357	548	621	331	363	287	4.6	4.2	8.9	2.2	5.2	bd	2.2	3.8	20.6	11.7	9.6	3.7
40		6.2	4.1	4.3	5.8	4.9	6.5	918	881	1102	631	545	581	9.5	2.5	10.5	3.5	6.3	bd	3.0	5.2	7.4	11.6	11.6	5.4
80		6.3	4.3	4.2	6.0	4.7	6.5	1916	1570	2576	1137	994	588	6.2	1.3	12.5	2.7	5.3	bd	2.0	8.2	4.4	15.2	12.1	6.1
160		5.8	4.5	4.5	6.2	5.2	6.5	1963	2604	3917	2500	1904	2306	6.3	2.9	11.5	4.2	5.5	bd	5.7	10.4	12.7	20.7	15.7	13.6
320		6.6	5.0	5.2	6.2	6.9	6.5	3487	5327	5511	3382	4000	4758	4.3	4.0	10.0	6.1	6.4	bd	11.9	20.2	17.0	25.1	21.7	28.3
0	14	6.1	4.3	4.0	5.1	6.3	6.5	345	395	7.6	43.4	123	37.5	6.2	3.7	20.2	1.0	6.7	bd	1.6	3.8	3.3	11.4	11.1	5.6
20		6.2	4.4	4.2	5.6	6.3	6.5	367	107	670	342.1	243	288	6.5	2.9	13.2	2.5	7.6	bd	0.9	1.6	7.1	13.5	12.3	5.9
40		6.4	4.6	4.3	5.8	6.3	6.4	643	859	1135	653	475	581	4.1	3.6	11.5	2.9	8.1	bd	1.7	4.5	9.3	15.7	13.0	6.9
80		6.0	5.2	4.5	6.2	6.0	6.1	1378	1525	2551	1207	926	1136	5.9	2.0	12.5	1.6	7.6	bd	2.9	8.2	12.4	17.4	14.5	11.2
160		4.9	4.0	4.8	6.2	4.3	6.6	3094	2707	3614	2312	1834	2252	6.3	2.8	10.2	3.7	7.0	bd	5.5	13.0	18.7	21.3	16.3	16.4
320		6.0	4.7	5.2	6.3	6.5	6.5	5507	5174	5291	3452	3687	45901	6.4	1.8	9.9	1.3	5.1	bd	13.3	21.2	21.0	27.9	20.9	26.6

bd below detection.

**Appendix 8.2. (contd.)** Final pH and concentrations of 0.05 M CaCl<sub>2</sub>-extractable metals in incubated Bonheim (Bo), Hutton, (Hu), Inanda (Ia), Longlands (Lo), Shortlands (Sd) and Valsrivier (Va) soil after the addition of electro-winning waste at rates of 0, 20, 40, 80, 160 and 320 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	pH						Mn						Fe						Co					
		Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va
0	28	6.3	4.1	4.0	5.0	6.3	6.5	423	244	18.2	49.8	147	63.7	6.2	2.3	18.3	1.6	7.6	bd	2.3	2.3	4.3	13.3	13.4	bd
20		6.3	4.2	4.2	5.7	6.3	6.4	521	373	682	328	260	323	6.1	2.7	12.5	1.8	7.0	bd	0.5	2.1	5.8	14.1	14.1	6.1
40		6.0	4.5	4.3	5.7	6.0	6.4	588	781	1379	758	360	603	6.5	2.5	12.9	3.7	7.8	bd	2.5	3.3	7.6	18.0	15.7	7.4
80		6.4	4.1	4.5	5.7	6.3	6.4	1053	1265	2169	1259	852	1228	2.3	3.9	4.5	2.6	3.5	bd	1.7	13.1	6.8	7.7	1.9	6.2
160		6.1	4.1	4.8	6.2	6.5	6.2	2181	2802	3618	2176	1810	2307	3.0	2.7	3.6	2.1	2.3	bd	6.2	16.0	12.9	12.5	3.8	12.4
320		6.0	3.8	5.0	6.2	4.3	6.5	4769	5665	4936	3775	3869	4884	3.7	4.2	3.4	7.3	1.4	bd	15.2	19.7	21.6	19.2	10.7	20.2
0	56	6.2	4.1	4.0	4.8	6.3	6.6	327	198	8.7	40.6	160	60.6	4.2	2.3	13.8	1.8	2.5	bd	1.5	bd	bd	3.2	bd	bd
20		5.8	4.2	4.2	5.5	6.1	6.5	622	432	676	315	329	340	4.5	3.1	6.8	2.5	4.9	bd	1.3	1.2	2.4	4.8	bd	1.5
40		6.3	4.0	4.3	5.7	6.0	6.5	1000	694	1131	730	363	608	3.8	3.3	5.6	2.8	1.7	bd	0.5	bd	4.1	6.7	2.0	2.0
80		5.7	4.2	4.5	5.8	6.1	6.2	1221	1317	2013	1199	684	1320	4.7	3.2	4.7	1.6	2.6	bd	2.1	2.3	7.3	10.3	2.0	4.6
160		6.2	4.4	4.8	6.0	6.2	6.2	2221	2895	4354	2480	1642	2579	3.1	2.6	5.2	4.7	2.1	bd	4.4	11.9	14.0	14.9	3.5	11.8
320		6.1	4.3	5.4	6.1	6.1	6.3	6754	5439	5942	4245	3880	4799	3.2	1.9	5.4	3.2	2.0	bd	17.2	26.8	18.7	22.4	10.5	26.4
0	84	5.6	4.2	4.0	4.8	6.2	6.5	528	115	9.4	29.2	95.3	29.8	4.9	4.2	14.9	7.9	4.0	bd	1.5	2.2	0.6	4.4	1.6	bd
20		6.0	4.3	4.1	5.3	5.7	5.8	261	445	817	304	334	258	3.6	3.8	7.1	3.2	1.4	bd	1.2	bd	1.2	5.8	2.1	1.5
40		5.1	4.1	4.3	5.8	5.8	5.7	946	771	1166	704	414	406	3.7	2.7	6.8	2.6	2.8	bd	2.1	bd	4.4	8.1	3.3	bd
80		5.2	4.1	4.5	5.7	5.8	6.2	2016	1253	2056	1295	560	1366	5.8	3.1	6.3	8.8	3.8	bd	3.9	1.9	7.2	11.5	3.2	6.9
160		5.8	4.2	4.7	6.0	6.2	6.3	2457	3072	4782	2232	1729	2507	5.0	2.8	7.0	1.7	4.8	bd	4.8	10.9	15.0	16.8	4.4	12.4
320		6.3	4.2	5.2	6.0	6.2	6.3	4957	5543	5636	4463	3910	5009	4.3	1.4	6.9	8.3	2.9	bd	13.4	22.2	27.5	25.1	12.1	25.8
0	140	5.8	3.9	4.0	4.9	6.2	6.5	328	214	18.5	48.2	106	53.8	4.7	4.2	13.6	4.2	5.3	bd	1.8	bd	2.5	6.5	2.1	2.8
20		5.0	4.1	4.2	5.0	5.3	5.4	435	353	727	240	368	180	3.3	3.0	7.4	8.9	4.8	bd	bd	bd	2.9	5.5	4.8	2.0
40		5.6	3.8	4.2	5.6	5.1	5.2	971	671	1115	822	666	216	4.5	3.7	7.3	4.0	3.2	bd	1.6	bd	4.1	10.7	5.7	1.8
80		4.9	3.9	4.4	5.8	5.5	5.9	1937	920	2484	1209	530	1401	6.0	3.5	8.2	3.7	5.9	bd	3.7	1.0	8.1	14.2	5.9	6.5
160		5.8	4.2	4.8	5.9	5.9	6.2	2466	2818	3993	2920	1245	2638	3.6	2.9	5.8	6.8	4.5	bd	4.4	8.8	13.7	21.6	4.7	12.9
320		5.9	4.1	5.3	5.9	6.3	6.2	5752	5883	5267	4161	3899	5459	4.2	1.9	9.2	4.6	3.3	bd	12.5	25.8	37.6	7.9	11.3	28.5

bd below detection.



**Appendix 8.2. (contd.)**

Final pH and concentrations of 0.05 M CaCl<sub>2</sub>-extractable metals in an incubated Bonheim (Bo), Hutton, (Hu), Inanda (Ia), Longlands (Lo), Shortlands (Sd) and Valsrivier (Va) soils after the addition of electro-winning waste at rates of 0, 20, 40, 80, 160 and 320 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	Cu						Pb						Zn						Ni					
		Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va
0	0	2.2	2.1	bd	bd	bd	bd	6.7	2.7	bd	5.4	4.1	3.8	0.7	4.2	2.3	0.8	bd	2.7	bd	2.9	bd	bd	bd	bd
20		bd	0.7	bd	bd	bd	bd	5.7	2.1	bd	2.6	3.7	2.9	0.3	4.5	2.2	3.6	bd	2.5	bd	bd	1.3	bd	bd	bd
40		bd	bd	bd	bd	bd	bd	5.7	3.9	bd	3.7	2.3	bd	0.1	2.7	2.5	3.4	2.0	1.9	bd	2.2	1.2	2.4	2.0	bd
80		bd	bd	bd	bd	bd	bd	4.9	2.1	bd	2.5	4.0	2.9	2.6	5.8	3.1	3.3	1.9	2.1	bd	2.9	bd	3.6	2.7	bd
160		bd	bd	bd	bd	bd	bd	5.8	3.3	bd	4.7	6.0	2.2	1.8	2.6	3.2	3.1	1.3	2.7	2.6	2.9	1.8	bd	2.6	bd
320		bd	bd	bd	bd	bd	bd	6.1	bd	bd	4.7	bd	2.4	1.1	3.0	3.9	1.9	1.3	2.3	3.0	4.3	3.0	3.1	2.8	4.0
0	3	bd	bd	bd	bd	bd	bd	6.1	4.9	bd	3.7	2.5	bd	0.6	1.8	2.0	0.9	1.3	2.1	bd	0.4	1.7	bd	bd	bd
20		bd	bd	bd	bd	bd	bd	3.3	4.1	bd	5.2	4.3	3.4	0.6	3.7	2.0	0.9	1.6	2.4	1.1	bd	bd	bd	2.5	bd
40		bd	bd	bd	bd	bd	bd	5.0	3.0	bd	6.0	3.6	5.3	2.1	3.8	4.9	0.9	1.8	2.4	1.5	bd	2.0	bd	bd	bd
80		bd	1.6	bd	bd	bd	bd	8.2	4.1	1.1	8.3	5.6	5.4	1.8	6.2	5.7	1.0	1.1	4.0	1.8	3.0	4.5	2.3	4.3	bd
160		bd	bd	bd	bd	bd	bd	6.9	3.9	1.0	6.0	4.0	3.5	2.0	4.6	5.1	0.9	2.0	4.6	1.5	bd	3.8	bd	3.3	2.5
320		bd	bd	bd	bd	bd	bd	4.5	bd	bd	4.4	4.3	3.2	2.2	3.1	4.0	4.1	1.2	3.2	1.6	2.9	3.6	3.1	4.4	6.1
0	7	bd	bd	bd	bd	bd	bd	6.4	bd	1.2	6.4	6.0	3.8	0.5	3.1	1.4	2.7	bd	1.6	1.7	bd	1.5	bd	bd	bd
20		bd	bd	bd	bd	bd	bd	6.5	2.7	bd	7.6	2.8	4.9	0.8	3.4	3.7	1.2	bd	4.1	1.5	bd	3.6	bd	bd	bd
40		1.3	1.4	bd	bd	bd	bd	8.8	bd	bd	6.4	3.4	3.0	2.3	2.3	3.3	2.0	1.6	1.9	bd	2.1	2.2	bd	bd	bd
80		bd	bd	bd	bd	bd	bd	9.4	3.1	bd	7.4	3.8	2.8	0.5	3.1	2.9	2.0	1.8	1.7	1.7	bd	bd	bd	2.9	2.4
160		bd	bd	bd	bd	bd	bd	4.7	bd	bd	9.2	8.4	4.4	2.5	3.8	4.8	1.4	2.3	3.3	2.9	3.4	3.0	5.7	3.1	4.5
320		bd	bd	bd	bd	bd	bd	4.8	bd	bd	6.0	6.1	3.4	3.1	3.4	4.5	1.1	2.4	5.1	2.4	2.3	1.9	3.3	5.2	6.2
0	14	bd	1.4	bd	bd	bd	bd	3.8	4.0	1.2	7.3	4.1	4.6	0.8	4.7	2.3	2.5	bd	2.5	1.8	3.3	1.7	2.5	2.9	bd
20		bd	bd	bd	bd	bd	bd	3.2	3.7	bd	6.1	4.6	5.1	0.7	3.5	3.0	3.9	1.1	6.0	bd	bd	1.6	bd	3.1	2.7
40		bd	bd	bd	bd	bd	bd	3.9	bd	1.5	8.6	2.7	3.5	1.6	3.9	2.9	3.0	1.5	3.3	bd	bd	bd	bd	4.0	2.5
80		bd	bd	bd	bd	bd	bd	4.5	3.4	bd	9.5	4.4	5.1	1.3	4.3	4.0	3.3	2.5	6.1	2.9	2.8	2.5	2.4	3.6	bd
160		bd	bd	bd	bd	bd	bd	5.3	2.1	bd	8.4	4.2	4.6	1.7	3.2	4.9	1.6	2.7	2.7	2.9	4.0	4.1	3.0	3.3	3.9
320		bd	bd	bd	bd	bd	bd	4.7	bd	bd	8.5	6.2	3.0	3.6	4.8	4.5	2.5	2.1	4.1	2.7	4.1	3.4	3.4	3.2	5.6

bd below detection.

# Appendix 8.2. (contd.)

Final pH and concentrations of 0.05 M CaCl<sub>2</sub>-extractable metals in an incubated Bonheim (Bo), Hutton, (Hu), Inanda (Ia), Longlands (Lo), Shortlands (Sd) and Valsrivier (Va) soil after the addition of electro-winning waste at rates of 0, 20, 40, 80, 160 and 320 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	Cu						Pb						Zn						Ni					
		Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va	Bo	Hu	Ia	Lo	Sd	Va
0	28	bd	bd	bd	bd	bd	bd	4.0	bd	bd	7.7	4.2	4.2	0.7	2.8	1.6	3.7	bd	1.9	bd	bd	1.8	2.2	2.0	2.8
20		bd	bd	bd	bd	bd	bd	7.7	bd	1.5	9.4	7.5	4.6	1.7	3.8	2.4	1.3	1.1	9.1	bd	3.8	2.3	bd	3.1	2.9
40		bd	bd	bd	bd	bd	bd	5.9	bd	bd	8.9	6.5	6.8	2.4	2.4	3.6	1.4	2.5	3.3	1.6	bd	1.9	bd	5.1	3.5
80		bd	3.3	bd	1.7	bd	bd	3.7	3.8	bd	2.7	3.2	bd	1.2	3.8	4.9	1.7	2.9	2.7	1.5	bd	3.0	bd	bd	bd
160		bd	1.3	bd	1.5	bd	bd	2.3	bd	1.0	2.2	1.3	bd	bd	5.0	6.0	1.6	3.8	2.7	1.2	bd	3.0	2.6	bd	2.4
320		bd	0.9	bd	1.3	bd	bd	1.6	bd	bd	1.7	2.2	bd	3.2	4.4	3.5	1.2	3.2	3.6	4.5	3.9	bd	4.4	bd	3.1
0	56	bd	0.7	bd	1.3	bd	bd	2.7	2.4	bd	2.4	2.1	bd	bd	2.1	1.3	1.4	1.9	4.7	bd	bd	bd	bd	bd	bd
20		bd	0.8	bd	1.5	bd	bd	5.1	1.8	bd	2.5	1.8	bd	bd	6.8	2.4	3.0	1.4	2.3	bd	bd	bd	bd	bd	bd
40		bd	0.7	bd	1.8	bd	bd	4.6	1.6	1.6	2.9	2.6	bd	0.4	5.3	3.0	1.5	1.7	2.9	bd	bd	bd	2.5	bd	bd
80		bd	0.7	bd	1.6	bd	bd	3.3	2.8	4.0	4.2	2.3	2.6	1.1	4.3	3.7	2.0	2.7	4.9	bd	bd	bd	bd	bd	bd
160		bd	bd	bd	1.8	bd	bd	1.7	bd	bd	3.6	4.3	2.0	2.0	3.6	3.8	1.8	3.2	4.3	3.1	bd	2.4	bd	bd	bd
320		bd	0.8	bd	1.8	bd	bd	3.9	bd	1.1	1.7	2.5	bd	1.1	4.5	4.2	1.4	4.7	3.3	3.3	bd	2.4	3.6	3.1	4.6
0	84	bd	2.1	bd	2.4	bd	bd	bd	3.6	3.1	1.8	1.6	bd	1.0	4.5	2.5	1.6	1.1	2.5	2.2	bd	2.0	bd	bd	bd
20		bd	bd	bd	1.9	bd	bd	bd	2.3	1.7	2.9	3.5	2.1	1.0	5.0	2.2	1.5	1.4	4.3	bd	bd	1.2	bd	bd	bd
40		1.6	1.3	bd	2.0	bd	bd	4.8	3.2	bd	5.5	3.3	2.9	5.7	4.5	4.7	1.4	2.5	3.3	2.5	bd	1.2	bd	bd	bd
80		bd	1.1	bd	2.5	bd	bd	3.7	2.7	1.3	2.7	3.7	3.1	2.3	6.0	4.0	3.0	2.7	3.8	2.9	bd	bd	4.2	bd	bd
160		bd	1.1	bd	2.3	bd	bd	4.3	2.1	1.9	4.2	2.4	2.4	2.0	7.6	4.0	2.8	3.5	4.1	1.8	2.6	2.3	4.5	bd	bd
320		bd	bd	bd	2.2	bd	bd	1.0	bd	bd	4.0	4.5	bd	1.9	5.4	5.4	1.5	4.8	6.4	4.6	bd	1.2	bd	2.3	3.8
0	140	bd	0.6	bd	2.3	bd	bd	3.7	bd	2.4	3.6	5.9	3.3	0.3	2.5	1.5	1.4	2.0	2.5	bd	bd	bd	bd	bd	bd
20		bd	0.7	bd	2.7	bd	bd	bd	3.8	1.6	3.4	5.2	5.5	2.4	4.5	3.0	1.8	2.9	3.3	2.0	bd	bd	bd	bd	bd
40		bd	0.7	bd	2.5	bd	bd	bd	bd	bd	4.3	5.9	4.7	1.5	4.7	3.3	5.4	2.8	2.9	bd	bd	1.5	bd	bd	bd
80		1.3	2.4	bd	2.9	bd	bd	1.7	3.9	bd	7.3	5.4	6.3	2.8	8.9	4.6	4.7	3.2	4.7	4.6	3.7	3.3	bd	bd	2.2
160		bd	1.1	bd	2.7	bd	bd	1.5	bd	2.6	5.2	9.0	5.3	2.2	7.6	4.0	1.7	5.3	4.2	3.9	bd	2.4	3.3	bd	2.3
320		1.4	1.3	bd	2.6	bd	bd	1.4	bd	1.4	3.8	7.3	5.2	2.3	7.5	2.2	2.8	4.9	4.0	4.3	4.0	1.6	bd	2.4	5.6

bd below detection.

**Appendix 8.3** Inorganically (IB), organically (OB) and amorphous oxide (AMOX)-bound metals extracted from an incubated Hutton soil after the addition of slag from the Samancor Mn-smelter at rates of 0, 30, 60, 120, 240 and 480 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	Mn			Fe			Co		
		IB	OB	AMOX	IB	OB	AMOX	IB	OB	AMOX
0	0	93.2	339	460	bd	815	16398	bd	20.5	41.9
30		6518	1349	1453	14.6	823	15694	bd	22.4	bd
60		8820	1445	2097	36.1	823	14082	bd	19.2	bd
120		15637	1974	4150	82.2	738	12663	bd	29.2	bd
240		23770	3728	6412	72.3	585	11512	bd	21.7	bd
480		43434	4035	15104	191	411	9482	bd	21.4	bd
0	3	119	421	504	bd	992	15596	bd	19.9	48.4
30		4915	1498	1882	bd	767	14592	bd	22.2	bd
60		7090	1321	2250	bd	671	13691	bd	38.2	bd
120		14127	1713	4800	bd	590	16465	bd	33.7	bd
240		24055	2991	8523	34.4	583	12824	bd	30.1	bd
480		34332	3021	11506	172	323	8454	bd	23.1	bd
0	7	209	481	668	bd	746	12140	bd	32.2	46.8
30		5292	1175	1859	bd	689	15972	bd	33.1	bd
60		8907	1514	3038	bd	760	15212	bd	34.3	bd
120		10270	2245	5397	bd	741	13319	bd	27.2	bd
240		23691	2660	10662	37.2	436	13240	bd	27.1	bd
480		36206	2931	16793	271	286	9150	bd	25.2	bd
0	14	141	602	627	bd	960	11459	bd	46.8	76.9
30		3886	1200	2024	bd	744	15914	bd	46.3	bd
60		4036	1342	3497	bd	694	18360	bd	32.2	bd
120		12552	1584	5878	bd	586	13912	bd	27.7	bd
240		24477	2614	10671	60.8	336	12818	bd	31.2	bd
480		36224	3592	16615	46.8	424	11014	bd	30.8	bd

bd below detection.

**Appendix 8.3. (contd.)** Inorganically (IB), organically (OB) and amorphous oxide (AMOX)-bound metals extracted from an incubated Hutton soil after the addition of slag from the Samancor Mn-smelter at rates of 0, 30, 60, 120, 240 and 480 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	Mn			Fe			Co		
		IB	OB	AMOX	IB	OB	AMOX	IB	OB	AMOX
0	28	157	729	583	bd	862	13576	bd	41.2	46.1
30		2864	1164	2402	bd	872	16853	bd	32.5	bd
60		6585	1729	3337	bd	1201	16166	bd	33.3	bd
120		11498	1669	9081	bd	510	11824	bd	28.5	bd
240		23684	1934	12721	27.0	358	10329	bd	29.9	bd
480		33960	2871	18558	186	208	9965	bd	24.2	bd
0	56	128	506	599	bd	1090	19467	bd	42.2	49.4
30		4331	1278	2655	bd	646	12089	bd	12.3	bd
60		7944	1073	6601	bd	547	11191	bd	7.9	bd
120		10465	1384	10240	bd	289	11123	bd	1.5	bd
240		23772	1961	10699	40.9	263	10195	bd	9.4	bd
480		33668	3231	15526	124	265	7967	bd	4.0	bd
0	84	50.0	707	796	bd	938	17671	bd	24.0	61.9
30		3515	1310	2795	bd	954	12688	bd	15.3	bd
60		7856	1234	3997	bd	503	11843	bd	4.4	bd
120		11931	1926	5784	bd	389	11055	bd	4.9	bd
240		20071	1568	8638	31.8	165	10214	bd	12.3	bd
480		34714	2046	12804	154	111	7603	bd	0.5	bd
0	140	85.3	748	638	bd	834	21527	bd	26.7	62.5
30		3615	806	2634	bd	571	11798	bd	3.5	bd
60		5603	761	4563	bd	461	10729	bd	bd	bd
120		9315	972	6412	bd	235	11203	bd	bd	bd
240		27266	1706	10030	31.0	163	9145	bd	3.4	bd
480		37093	2064	10095	43.8	115	8171	bd	6.0	bd

bd below detection.

**Appendix 8.3. (contd.)**

Inorganically (IB), organically (OB) and amorphous oxide (AMOX)-bound metals extracted from an incubated Hutton soil after the addition of slag from the Samancor Mn-smelter at rates of 0, 30, 60, 120, 240 and 480 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	Zn			Cu			Pb			Ni		
		IB	OB	AMOX	IB	OB	AMOX	IB	OB	AMOX	IB	OB	AMOX
0	0	bd	25.9	bd	bd	23.0	bd	bd	19.1	bd	bd	0.5	bd
30		bd	3.9	bd	bd	13.6	bd	bd	16.6	bd	bd	0.5	bd
60		bd	20.7	bd	bd	15.7	bd	bd	20.2	bd	bd	bd	bd
120		bd	6.9	bd	bd	13.8	bd	bd	17.8	bd	bd	5.4	bd
240		bd	5.5	bd	bd	13.1	bd	10.1	22.2	bd	bd	1.5	bd
480		bd	7.0	bd	bd	12.9	bd	14.6	22.4	bd	bd	3.5	bd
0	3	bd	7.5	bd	bd	9.0	bd	bd	bd	bd	bd	bd	bd
30		bd	7.4	bd	bd	15.8	bd	bd	13.8	bd	bd	bd	bd
60		bd	11.8	bd	bd	26.0	bd	bd	40.2	bd	bd	2.9	bd
120		bd	18.8	bd	bd	16.4	bd	bd	18.4	bd	bd	bd	bd
240		12.5	10.5	bd	bd	16.5	bd	bd	1.0	bd	bd	10.5	bd
480		10.8	6.9	bd	bd	10.8	bd	10.1	3.9	bd	bd	bd	bd
0	7	bd	9.9	bd	bd	5.5	bd	bd	6.0	bd	bd	7.4	bd
30		bd	9.9	bd	bd	15.8	bd	bd	6.9	bd	bd	bd	bd
60		bd	7.5	bd	bd	18.4	bd	bd	14.4	bd	bd	1.5	bd
120		bd	9.4	bd	bd	16.8	bd	bd	7.4	bd	bd	4.0	bd
240		21.1	16.2	bd	bd	14.3	bd	bd	10.3	bd	bd	bd	bd
480		4.9	22.7	bd	bd	16.3	bd	16.7	15.8	bd	bd	6.9	bd
0	14	bd	24.4	bd	bd	17.9	bd	bd	26.4	bd	bd	15.4	bd
30		bd	26.9	bd	bd	43.3	bd	bd	32.9	bd	bd	bd	bd
60		bd	23.1	bd	bd	20.1	bd	bd	12.6	bd	bd	bd	bd
120		bd	12.4	bd	bd	19.8	bd	bd	19.3	bd	bd	bd	bd
240		16.7	9.9	bd	bd	15.8	bd	bd	16.8	bd	bd	bd	bd
480		13.3	10.3	bd	bd	16.1	bd	11.3	1.5	bd	bd	bd	bd

bd below detection.

Appendix 8.3. (contd.)

Inorganically (IB), organically (OB) and amorphous oxide (AMOX)-bound metals extracted from an incubated Hutton soil after the addition of slag from the Samancor Mn-smelter at rates of 0, 30, 60, 120, 240 and 480 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	Zn			Cu			Pb			Ni		
		IB	OB	AMOX	IB	OB	AMOX	IB	OB	AMOX	IB	OB	AMOX
0	28	bd	42.6	bd	bd	11.3	bd	bd	bd	bd	bd	3.9	bd
30		bd	12.3	bd	bd	21.7	bd	bd	28.6	bd	bd	bd	bd
60		bd	12.4	bd	bd	25.3	bd	bd	12.9	bd	bd	bd	bd
120		bd	10.0	bd	bd	21.5	bd	bd	17.5	bd	bd	2.5	bd
240		13.1	8.0	bd	bd	19.5	bd	bd	22.5	bd	bd	bd	bd
480		12.1	4.9	bd	bd	18.2	bd	18.7	43.4	bd	bd	12.3	bd
0	56	bd	25.0	bd	bd	8.8	bd	bd	bd	bd	bd	4.4	bd
30		bd	2.0	bd	bd	15.3	bd	bd	16.8	bd	bd	bd	bd
60		bd	0.5	bd	bd	17.8	bd	bd	22.7	bd	bd	bd	bd
120		bd	1.5	bd	bd	13.6	bd	bd	18.1	bd	bd	bd	bd
240		bd	bd	bd	bd	9.9	bd	11.1	16.8	bd	bd	bd	bd
480		bd	15.5	bd	bd	24.5	bd	14.0	12.5	bd	bd	bd	bd
0	84	bd	19.0	bd	bd	26.5	bd	bd	31.5	bd	bd	6.5	bd
30		bd	3.9	bd	bd	23.1	bd	bd	9.4	bd	bd	0.5	bd
60		bd	6.4	bd	bd	15.7	bd	bd	15.7	bd	bd	bd	bd
120		15.1	2.0	bd	bd	16.8	bd	bd	25.7	bd	bd	bd	bd
240		bd	bd	bd	bd	21.7	bd	13.3	46.4	bd	bd	bd	bd
480		bd	5.0	bd	bd	14.4	bd	14.7	28.7	bd	bd	bd	bd
0	140	10.9	34.1	bd	bd	19.3	bd	bd	21.7	bd	bd	6.9	bd
30		bd	bd	bd	bd	18.2	bd	bd	6.4	bd	bd	bd	bd
60		10.7	bd	bd	bd	18.6	bd	bd	9.6	bd	bd	bd	bd
120		bd	bd	bd	bd	14.3	bd	bd	17.7	bd	bd	bd	bd
240		bd	3.4	bd	bd	16.1	bd	9.7	16.6	bd	bd	6.4	bd
480		12.9	bd	bd	bd	16.5	bd	12.1	5.0	bd	bd	2.0	bd

bd below detection.

**Appendix 8.4** Inorganically (IB), organically (OB) and amorphous oxide (AMOX)-bound metals extracted from an incubated Hutton soil after the addition of electro-winning waste at rates of 0, 20, 40, 80, 160 and 320 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	Mn			Fe			Co		
		IB	OB	AMOX	IB	OB	AMOX	IB	OB	AMOX
0	0	93.2	339	460	bd	815	16398	bd	20.5	41.9
20		577	690	3551	bd	830	20665	bd	10.5	40.8
40		1401	1239	9794	bd	804	24412	bd	9.7	63.0
80		2382	2230	20466	bd	874	28779	bd	24.8	60.6
160		7120	3434	22465	85.0	892	44771	42.6	29.7	62.4
320		9032	8221	28202	250	965	74253	60.2	63.0	83.5
0	3	119	421	504	bd	992	15596	bd	19.9	48.4
20		828	910	3691	bd	940	15567	bd	23.2	57.0
40		1395	1356	11896	bd	953	23659	bd	23.9	58.9
80		2960	2278	22079	bd	989	27861	21.5	44.9	81.8
160		5364	3597	21001	87.8	836	40940	36.1	35.5	60.3
320		9708	6834	25154	330	934	65792	67.7	54.3	68.4
0	7	209	481	668	bd	746	12140	bd	32.2	46.8
20		1046	1227	6368	bd	1082	14814	bd	32.8	48.2
40		1469	1481	7629	bd	925	17782	bd	36.1	49.8
80		4402	2803	14188	bd	1091	23723	18.3	41.3	61.6
160		5503	3821	14701	55.0	978	35249	30.1	42.9	58.1
320		11214	7058	22515	358	1058	52701	79.1	57.9	84.1
0	14	141	602	6278	bd	960	11459	bd	46.8	76.9
20		644	1382	2926	bd	1394	19606	bd	41.2	53.2
40		1365	1817	12213	bd	1165	22737	bd	37.5	53.8
80		2908	2911	24455	bd	1288	31303	bd	41.8	66.0
160		6600	5432	21780	86.6	1366	44221	39.6	64.0	54.9
320		9342	9692	30600	523	1416	82093	98.3	78.3	60.9

bd below detection.

**Appendix 8.4. (contd.)** Inorganically (IB), organically (OB) and amorphous oxide (AMOX)-bound metals extracted from an incubated Hutton soil after the addition of electro-winning waste at rates of 0, 20, 40, 80, 160 and 320 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	Mn			Fe			Co		
		IB	OB	AMOX	IB	OB	AMOX	IB	OB	AMOX
0	28	157	729	583	bd	862	13576	bd	41.2	46.1
20		1083	1203	5584	bd	924	22138	bd	5bd	66.2
40		1176	1612	9809	bd	853	22032	bd	44.5	60.3
80		2484	2620	18886	bd	906	27254	bd	68.3	65.9
160		4676	4294	25086	60.2	981	44168	30.2	63.7	59.8
320		10307	7282	34106	260	1019	102286	58.6	80.0	54.9
0	56	128	506	599	bd	1090	19467	bd	42.2	49.4
20		869	1222	6039	bd	1229	21551	bd	56.9	75.6
40		1373	2594	16866	bd	2021	30144	bd	54.8	73.2
80		2771	2430	23685	bd	1271	30742	bd	62.6	93.9
160		4662	4044	20970	86.4	1089	54050	35.3	68.9	58.6
320		16347	7877	26544	277	1264	77794	57.6	91.5	69.1
0	84	50.0	707	796	bd	938	17671	bd	24.0	61.9
20		535	1374	2834	bd	1309	16265	bd	16.9	73.3
40		1146	2105	10753	bd	1349	25694	bd	21.7	83.5
80		2506	2904	19414	bd	1359	27948	bd	28.9	84.6
160		4738	5307	23493	30.2	1262	55978	22.0	34.3	74.1
320		10232	9843	29530	261	1384	91535	64.5	60.5	88.6
0	140	85.3	748	638	bd	834	21527	bd	26.7	62.5
20		507	1283	5223	bd	1239	19717	bd	21.5	80.0
40		977	1629	11273	bd	1163	29666	bd	16.8	85.7
80		2521	2232	26213	bd	1253	36424	bd	34.6	95.1
160		4499	4581	32341	41.5	1205	66185	23.1	40.6	82.0
320		9681	7694	26790	220	1127	77071	53.1	50.0	87.1

bd below detection.



**Appendix 8.4. (contd.)** Inorganically (IB), organically (OB) and amorphous oxide (AMOX)-bound metals extracted from an incubated Hutton soil after the addition of electro-winning waste at rates of 0, 20, 40, 80, 160 and 320 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	Zn			Cu			Pb			Ni		
		IB	OB	AMOX	IB	OB	AMOX	IB	OB	AMOX	IB	OB	AMOX
0	0	bd	25.9	bd	bd	23.0	bd	bd	19.1	bd	bd	0.5	bd
20		bd	20.4	bd	bd	11.0	bd	bd	bd	bd	bd	bd	bd
40		10.0	22.2	bd	bd	14.5	bd	bd	4.4	bd	bd	4.8	bd
80		19.9	13.4	bd	bd	15.4	bd	bd	3.0	bd	bd	bd	bd
160		37.3	17.1	bd	6.4	22.4	52.8	bd	1.9	bd	bd	1.9	bd
320		58.6	27.6	bd	15.3	37.4	86.7	bd	69.4	123	12.0	12.3	bd
0	3	bd	7.5	bd	bd	9.0	bd	bd	bd	bd	bd	bd	bd
20		bd	19.7	bd	bd	10.4	bd	bd	bd	bd	bd	2.0	bd
40		11.6	25.9	bd	bd	13.4	bd	bd	2.0	bd	bd	0.5	bd
80		18.1	26.6	bd	bd	28.6	47.1	bd	33.0	bd	bd	9.9	bd
160		33.4	37.5	bd	5.9	20.0	47.8	bd	16.0	bd	bd	9.5	bd
320		69.8	30.9	bd	18.3	38.3	82.2	11.4	99.1	153	10.5	3.5	bd
0	7	bd	9.9	bd	bd	5.5	bd	bd	6.0	bd	bd	7.4	bd
20		bd	12.6	bd	bd	9.1	bd	bd	9.1	bd	bd	bd	bd
40		16.8	18.0	bd	bd	10.0	bd	bd	35.6	bd	bd	3.5	bd
80		17.8	21.4	bd	bd	17.4	36.6	bd	39.4	bd	bd	5.0	bd
160		30.6	28.3	bd	4.3	21.9	53.8	bd	58.0	bd	bd	bd	bd
320		74.8	32.9	bd	18.8	40.9	121	12.3	43.9	127	11.7	15.5	bd
0	14	bd	24.4	bd	bd	17.9	bd	bd	26.4	bd	bd	15.4	bd
20		bd	15.6	bd	bd	11.0	bd	bd	bd	bd	bd	7.0	bd
40		9.9	15.8	bd	bd	13.3	bd	bd	bd	bd	bd	3.9	bd
80		18.8	18.9	bd	bd	15.4	38.4	bd	5.0	bd	bd	5.5	bd
160		34.5	31.5	bd	7.4	36.9	55.2	bd	bd	bd	bd	2.5	bd
320		88.8	41.4	bd	26.1	53.4	89.3	12.8	36.9	155.3	13.7	16.5	bd

bd below detection.

**Appendix 8.4. (contd.)** Inorganically (IB), organically (OB) and amorphous oxide (AMOX)-bound metals extracted from an incubated Hutton soil after the addition of electro-winning waste at rates of 0, 20, 40, 80, 160 and 320 g kg<sup>-1</sup>. Metal concentrations are expressed in mg kg<sup>-1</sup>

Application rate (g kg <sup>-1</sup> )	Sampling day	Zn			Cu			Pb			Ni		
		IB	OB	AMOX	IB	OB	AMOX	IB	OB	AMOX	IB	OB	AMOX
0	28	bd	42.6	bd	bd	11.3	bd	bd	bd	bd	bd	3.9	bd
20		bd	44.5	bd	bd	11.0	bd	bd	3.5	bd	bd	bd	bd
40		bd	17.3	bd	bd	10.4	bd	bd	2.5	bd	bd	9.9	bd
80		18.2	27.6	bd	bd	26.6	38.2	bd	26.1	bd	bd	9.0	bd
160		27.6	27.0	bd	5.2	27.0	52.4	bd	29.9	bd	bd	3.4	bd
320		62.8	36.1	bd	15.4	45.0	86.6	10.1	67.7	170	10.7	6.9	bd
0	56	bd	25.0	bd	bd	8.8	bd	bd	bd	bd	bd	4.4	bd
20		bd	18.0	bd	bd	12.5	32.1	bd	1.5	bd	bd	12.0	bd
40		bd	28.7	bd	bd	23.2	34.7	bd	bd	bd	bd	9.9	bd
80		25.6	26.8	bd	bd	21.4	47.8	bd	5.0	bd	bd	11.9	bd
160		30.0	28.2	bd	5.6	25.7	55.0	bd	34.2	bd	bd	4.5	bd
320		60.6	43.2	bd	15.1	55.2	103	10.5	96.9	121	11.0	10.9	bd
0	84	bd	19.0	bd	bd	26.5	bd	bd	31.5	bd	bd	6.5	bd
20		bd	11.4	bd	bd	21.4	43.5	bd	17.4	bd	bd	bd	bd
40		bd	15.3	bd	bd	22.6	34.4	bd	17.2	bd	bd	3.4	bd
80		24.5	15.4	bd	bd	30.9	41.3	bd	23.4	bd	bd	7.5	bd
160		32.6	15.6	bd	5.2	42.3	50.4	bd	60.0	bd	bd	6.6	bd
320		64.2	31.5	bd	18.2	69.5	95.0	bd	72.5	156	12.4	5.5	bd
0	140	10.9	34.1	bd	bd	19.3	bd	bd	21.7	bd	bd	6.9	bd
20		16.8	10.0	bd	bd	20.5	bd	bd	15.5	bd	bd	7.5	bd
40		99.7	7.4	bd	bd	18.8	40.9	bd	20.8	bd	bd	2.5	bd
80		12.2	17.8	bd	bd	41.2	44.2	bd	47.8	bd	bd	9.1	bd
160		25.7	19.3	bd	5.6	42.1	59.8	bd	86.1	bd	bd	10.4	bd
320		56.9	29.9	bd	15.5	60.8	94.7	bd	84.8	126	8.7	11.3	bd

bd below detection.

**Appendix 8.5.**      Assay (as supplied) of the humic acid used in Chapters 8 and 9

S100 Humic Acid

Typical analysis:

<b>Parameter (Total)</b>	<b>% (dry basis)</b>
Soluble potassium humate and fulvate	92.0
Humic and fulvic acid	78.0
Organic carbon	67.5
K	13.0
N	0.3
Ca	0.12
Mg	0.2
S	0.3
Na	0.48
P	0.12
Fe	0.3
Si	1.3
	<b>ppm</b>
Mn	5.0
Zn	15.0
Cu	18.0
Co	10.4
B	5.5
Mo	1.2
Cd	< 0.5
Hg	0.6
Pb	< 5
As	< 2
Cr	14.0
Ni	13.0
pH (water)	10.0
Bulk density (g cm <sup>-3</sup> )	0.94

**Appendix 9.1**

Concentrations of nutrients in ryegrass foliage from Harvest 1 (H1) and Harvest 2 (H2) grown in either a Longlands or Hutton soil treated with slag from the Samancor Mn-smelter at rates of 0, 30, 60, 120, 240 and 480 g kg<sup>-1</sup>. The adequate and critical concentrations for ryegrass (Miles, 1994) are also given

Soil	Application rate (g kg <sup>-1</sup> )	Ca		Mg		K		N		P		S		Na	
		H1	H2	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2
		------(%)-----												-----(mg kg <sup>-1</sup> )----	
Longlands	0	0.55	0.34	0.24	0.14	2.62	1.08	0.78	1.15	0.14	0.12	0.24	0.13	2584	1558
	30	0.56	0.40	0.29	0.17	2.67	1.54	0.65	1.19	0.29	0.17	0.25	0.18	3898	1457
	60	0.57	0.59	0.26	0.24	2.76	2.43	0.65	1.17	0.25	0.18	0.24	0.26	3658	2515
	120	0.58	0.40	0.28	0.15	3.56	1.62	1.00	1.50	0.16	0.09	0.29	0.15	3627	1695
	240	0.53	0.42	0.22	0.14	4.99	2.60	0.98	2.41	0.11	0.08	0.29	0.20	2949	2313
	480	nd	0.28	nd	0.13	nd	1.58	nd	nd	nd	0.05	nd	0.15	nd	2240
Hutton	0	0.45	0.43	0.37	0.33	3.33	2.07	1.64	0.68	0.17	0.24	0.34	0.45	1513	1117
	30	0.45	0.42	0.33	0.35	2.91	1.86	0.97	0.99	0.22	0.28	0.32	0.56	1222	933
	60	0.53	0.51	0.37	0.37	2.78	1.46	0.90	0.98	0.21	0.26	0.35	0.48	2744	2570
	120	0.56	0.44	0.32	0.23	2.85	1.34	0.90	0.98	0.22	0.17	0.34	0.31	3237	2182
	240	0.60	0.55	0.27	0.25	2.85	1.89	0.94	1.06	0.19	0.16	0.29	0.35	2846	1666
	480	0.57	0.41	0.23	0.15	3.72	1.41	1.16	1.44	0.18	0.06	0.33	0.20	1738	1266
Miles (1994)	Adequate	0.26-1.0		0.2-0.5		2.5-6.0		3.6-6.0		0.25-0.36		0.25-0.32			
	Critical	0.25		0.10		2.0-3.0		3.5		0.24		0.20			
nd	not determined due to inadequate sample size														

**Appendix 9.2** Concentrations of trace nutrients and elements in ryegrass from Harvest 1 (H1) and Harvest 2 (H2) grown in either a Longlands or Hutton soil treated with slag from the Samancor Mn-smelter at rates of 0, 30, 60, 120, 240 and 480 g kg<sup>-1</sup>. The adequate and critical concentrations for ryegrass (Miles, 1994) are also given

Soil	Application rate (g kg <sup>-1</sup> )	Cu		Fe		Mn		Ni		Pb		Zn	
		H1	H2	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2
		(mg kg <sup>-1</sup> )											
Longlands	0	0.4	4.3	71.1	70.9	66.7	286	bd	3.5	bd	3.0	9.8	22.8
	30	4.6	5.8	81.8	79.7	970	1819	bd	4.6	bd	3.5	19.6	17.7
	60	2.7	9.0	100	78.3	790	2059	bd	7.3	bd	4.7	17.3	21.4
	120	2.8	7.2	137	89.4	345	677	bd	4.3	bd	4.1	13.6	16.3
	240	0.0	9.2	76.7	95.7	225	353	bd	5.4	bd	4.5	bd	23.6
	480	nd	6.9	nd	94.5	nd	200	nd	8.7	nd	6.0	nd	18.9
Hutton	0	4.9	6.3	145	82.4	65.9	327	bd	7.1	bd	4.1	33.0	31.4
	30	7.2	7.5	115	93.6	62.6	203	bd	5.5	bd	5.7	24.7	31.7
	60	6.4	6.7	178	81.8	196	529	bd	5.8	bd	7.7	29.7	30.0
	120	8.1	6.7	150	76.0	206	481	bd	4.8	bd	3.3	21.3	16.4
	240	10.8	7.7	105	81.1	317	754	bd	5.8	bd	3.7	21.2	20.6
	480	13.5	7.0	71.9	81.3	413	484	bd	3.2	bd	3.2	36.6	19.7
Miles (1994)	Adequate	6-12		50-70		50-300						15-20	
	Critical	5										10-13	
bd	below detection.												
nd	not determined.												

### Appendix 9.3

Concentrations of nutrients and trace elements in ryegrass from Harvest 1 (H1) and Harvest 2 (H2) grown in a Hutton soil treated with electro-winning waste from MMC at rates of 0, 20 and 40 g kg<sup>-1</sup>. The adequate and critical concentrations for ryegrass (Miles, 1994) are also given

Application rate (g kg <sup>-1</sup> )	Ca		Mg		K		N		P		S		Na	
	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2
	------(%)-----												----- (mg kg <sup>-1</sup> ) -----	
0	0.45	0.43	0.37	0.33	3.33	2.07	1.64	0.68	0.17	0.24	0.34	0.45	1513	1117
20	0.57	0.34	0.47	0.30	3.66	0.25	2.70	0.86	0.17	0.07	0.45	0.23	4377	2675
40	0.43	0.47	0.42	0.53	4.04	0.82	2.51	2.84	0.21	0.12	0.70	0.36	1785	5568
Adequate	0.26-1.0		0.2-0.5		2.5-6.0		3.6-6.0		0.25-0.36		0.25-0.32			
Critical	0.25		0.10		2.0-3.0		3.5		0.24		0.20			
Application rate (g kg <sup>-1</sup> )	Co		Cu		Fe		Mn		Ni		Pb		Zn	
	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2
	----- (mg kg <sup>-1</sup> ) -----													
0	bd	bd	4.87	6.31	145	82.4	65.9	326	bd	7.11	bd	4.12	33.0	31.4
20	bd	1.63	10.5	4.44	123	84.2	323	314	bd	5.55	bd	4.82	60.7	22.9
40	bd	1.75	12.7	13.2	132	115	1312	1929	bd	8.47	bd	5.28	78.0	63.2
Adequate	6-12				50-70				50-300				15-20	
Critical	5												10-13	

bd below detection.

**Appendix 9.4** The  $\text{pH}_{\text{water}}$ , electrical conductivity (EC) and 0.05 M  $\text{CaCl}_2$  extractable Mn concentration in a Hutton soil incubated for three weeks with electro-winning waste (EW) at 0, 10, 20 and 40  $\text{g kg}^{-1}$  with additional treatments of either humic acid and lime or compost and lime

EW application rate ( $\text{g kg}^{-1}$ )	Treatment	pH (water)	EC ( $\text{mS m}^{-1}$ )	Mn ( $\text{mg kg}^{-1}$ )
0		6.17	26.6	30.6
10	20 $\text{g kg}^{-1}$ humic acid + 0 $\text{Mg ha}^{-1}$ lime	5.61	84.5	68.9
20		5.44	151	102
40		5.34	243	270
0		6.42	29.3	25.5
10	20 $\text{g kg}^{-1}$ humic acid + 5 $\text{Mg ha}^{-1}$ lime	5.86	97.1	49.5
20		5.65	166	73.9
40		5.55	266	220
0		6.65	32.9	12.7
10	20 $\text{g kg}^{-1}$ humic acid + 10 $\text{Mg ha}^{-1}$ lime	6.08	107	38.5
20		5.87	176	55.3
40		5.73	254	123
0		5.52	25.5	44.9
10	20 $\text{g kg}^{-1}$ compost + 0 $\text{Mg ha}^{-1}$ lime	5.26	72.9	89.7
20		5.15	129	116
40		5.03	229	270
0		5.81	27.8	25.1
10	20 $\text{g kg}^{-1}$ compost + 5 $\text{Mg ha}^{-1}$ lime	5.47	85.5	72.1
20		5.34	144	79.8
40		5.27	230	190
0		6.10	30.0	22.8
10	20 $\text{g kg}^{-1}$ compost + 10 $\text{Mg ha}^{-1}$ lime	5.76	86.3	49.1
20		5.63	143	73.2
40		5.45	228	117
0		5.52	14.9	42.7
10	Control (No organic matter or lime)	5.23	57.5	85.9
20		5.05	126	123
40		4.98	225	283

**Appendix 9.5** Analysis of variance tables for yield from (a) Harvest 1, (b) Harvest 2 and (c) total yield of ryegrass grown in a Hutton soil treated with electro-winning waste from MMC at rates of 0, 10, 20 and 40 g kg<sup>-1</sup> and organic matter (either humic acid or compost) at 0 or 20 g kg<sup>-1</sup> with the organic matter treatments receiving lime at rates of 0, 5 and 10 Mg ha<sup>-1</sup>

(a)

Source of variation	df	SS	MS	VR	F Probability
Block (replicate)	2	0.012	0.01	46.24	
Organic matter/lime treatment	6	26.78	4.46	43.41	< 0.001
EW application rate	3	12.57	4.19	2.92	< 0.001
Treatment x EW rate	18	5.06	0.28		0.001
Residual	54	5.21	0.10		
Total	83	49.65			
Coefficient of variation (%)	0.6				

(b)

Source of variation	df	SS	MS	VR	F Probability
Block (replicate)	2	6.88	3.44	5.46	
Organic matter/lime treatment	6	14.54	2.42	3.85	0.003
EW application rate	3	393.73	131.24	208.41	< 0.001
Treatment x EW rate	18	20.38	1.13	1.80	0.050
Residual	54	34.01	0.63		
Total	83	469.54			
Coefficient of variation (%)	10.4				

(c)

Source of variation	df	SS	MS	VR	F Probability
Block (replicate)	2	6.40	3.20	4.77	
Organic matter/lime treatment	6	61.42	10.24	15.27	< 0.001
EW application rate	3	448.38	149.46	223.04	< 0.001
Treatment x EW rate	18	29.60	1.64	2.45	0.006
Residual	54	36.19	0.67		
Total	83	581.97			
Coefficient of variation (%)	6.6				

df degrees of freedom.  
MS mean sum of squares.  
SS sum of squares.  
VR variance ratio.



**Appendix 9.6** Concentrations of nutrients in ryegrass from Harvest 1 (H1) and Harvest 2 (H2) grown a Hutton soil treated with electro-winning waste (EW) from MMC at rates of 0, 10, 20 and 40 g kg<sup>-1</sup> and organic matter (either humic acid or compost) at 0 or 20 g kg<sup>-1</sup> with the organic matter treatments receiving lime at rates of 0, 5 and 10 Mg ha<sup>-1</sup>. The adequate and critical concentrations for ryegrass (Miles, 1994) are also given

EW application rate (g kg <sup>-1</sup> )	Treatment	Ca		Mg		K		P		N	
		H1	H2	H1	H2	H1	H2	H1	H2	H1	H2
		------(%)-----									
0	20 g kg <sup>-1</sup>	0.39	0.27	0.25	0.23	4.58	3.61	0.50	0.39	1.58	1.19
10	humic acid	0.41	0.25	0.29	0.22	5.23	2.88	0.33	0.30	2.99	1.01
20	+ 0 Mg ha <sup>-1</sup>	0.56	0.26	0.32	0.19	5.71	2.97	0.38	0.21	4.43	1.22
40	lime	0.44	0.28	0.28	0.24	7.09	3.85	0.25	0.11	4.74	2.14
0	20 g kg <sup>-1</sup>	0.47	0.28	0.22	0.22	3.96	3.56	0.39	0.32	1.74	1.14
10	humic acid	0.44	0.32	0.28	0.22	5.23	2.89	0.28	0.28	3.08	1.14
20	+ 5 Mg ha <sup>-1</sup>	0.48	0.30	0.31	0.23	6.01	3.01	0.32	0.18	4.35	1.09
40	lime	0.58	0.26	0.29	0.22	5.06	3.69	0.23	0.09	4.43	2.06
0	20 g kg <sup>-1</sup>	0.39	0.31	0.23	0.22	3.78	3.45	0.32	0.34	2.24	1.19
10	humic acid	0.47	0.40	0.26	0.24	4.74	3.63	0.25	0.24	3.50	1.10
20	+ 10 Mg ha <sup>-1</sup>	0.57	0.39	0.32	0.21	5.34	3.23	0.29	0.16	4.56	1.15
40	lime	0.54	0.29	0.27	0.19	5.17	3.39	0.31	0.08	4.71	2.14
0	20 g kg <sup>-1</sup>	0.51	0.47	0.30	0.28	3.68	2.34	0.50	0.26	2.07	1.01
10	compost	0.61	0.50	0.35	0.34	4.17	2.03	0.38	0.30	2.98	0.87
20	+ 0 Mg ha <sup>-1</sup>	0.71	0.56	0.39	0.37	4.18	1.95	0.36	0.29	4.18	0.96
40	lime	0.75	0.52	0.48	0.40	4.48	0.79	0.35	0.17	4.87	1.20
0	20 g kg <sup>-1</sup>	0.62	0.55	0.33	0.33	3.69	2.69	0.42	0.41	2.13	1.05
10	compost	0.72	0.60	0.38	0.41	3.43	2.55	0.34	0.40	3.16	1.04
20	+ 5 Mg ha <sup>-1</sup>	0.83	0.52	0.45	0.37	4.23	2.77	0.38	0.27	4.53	0.95
40	lime	0.79	0.51	0.41	0.38	4.33	1.74	0.43	0.18	4.76	1.40
0	20 g kg <sup>-1</sup>	0.55	0.52	0.26	0.29	4.10	3.40	0.45	0.39	2.30	1.04
10	compost	0.67	0.58	0.32	0.33	4.33	2.53	0.41	0.36	3.03	1.12
20	+ 10 Mg ha <sup>-1</sup>	0.78	0.55	0.42	0.34	4.85	2.18	0.32	0.32	4.50	1.05
40	lime	0.83	0.56	0.37	0.36	5.09	0.95	0.31	0.24	4.87	1.61
0	Control	0.57	0.48	0.30	0.30	3.98	3.01	0.43	0.34	1.86	1.15
10	(No organic	0.75	0.51	0.38	0.31	3.58	2.00	0.31	0.31	3.03	1.02
20	matter or	0.76	0.47	0.42	0.30	3.19	0.76	0.22	0.22	4.37	1.00
40	lime)	0.54	0.66	0.33	0.43	3.92	0.96	0.27	0.18	4.81	3.21
Miles (1994)	Adequate	0.26-1.0		0.2-0.5		2.5-6.0		0.25-0.36		3.6-6.0	
	Critical	0.25		0.10		2.0-3.0		0.24		3.5	

**Appendix 9.7** Concentrations of trace elements in ryegrass from Harvest 1 (H1) and Harvest 2 (H2) grown a Hutton soil treated with electro-winning waste (EW) from MMC at rates of 0, 10, 20 and 40 g kg<sup>-1</sup> and organic matter (either humic acid or compost) at 0 or 20 g kg<sup>-1</sup> with the organic matter treatments receiving lime at rates of 0, 5 and 10 Mg ha<sup>-1</sup>. The adequate and critical concentrations for ryegrass (Miles, 1994) are also given

EW application rate (g kg <sup>-1</sup> )	Treatment	Mn		Zn		Cu		Fe	
		H1	H2	H1	H2	H1	H2	H1	H2
		----- (mg kg <sup>-1</sup> ) -----							
0	20 g kg <sup>-1</sup>	76.0	201	44.9	21.7	15.1	9.64	110	55.5
10	humic acid	89.1	193	54.1	19.7	17.6	7.35	150	54.6
20	+ 0 Mg ha <sup>-1</sup>	139	179	61.7	25.2	19.2	8.69	147	69.2
40	lime	185	201	65.0	40.4	19.6	10.73	104	90.2
0	20 g kg <sup>-1</sup>	47.6	81.7	31.0	24.0	10.9	8.35	108	58.0
10	humic acid	71.2	109	49.7	28.5	14.9	8.98	154	71.1
20	+ 5 Mg ha <sup>-1</sup>	81.8	101	59.3	28.5	15.0	9.45	117	52.4
40	lime	163	144	63.3	47.1	18.0	11.5	126	73.9
0	20 g kg <sup>-1</sup>	62.3	97.7	31.1	30.2	11.7	9.68	167	197
10	humic acid	80.6	97.5	44.2	35.3	15.4	9.70	120	74.9
20	+ 10 Mg ha <sup>-1</sup>	102	90.0	65.8	35.7	19.2	13.3	222	112
40	lime	131	94.0	63.9	41.7	19.3	10.7	148	86.6
0	20 g kg <sup>-1</sup>	82.3	236	46.0	31.7	13.9	7.67	238	90.8
10	compost	119	442	60.5	41.3	15.8	8.13	139	90.9
20	+ 0 Mg ha <sup>-1</sup>	137	485	76.0	49.5	15.6	9.72	118	88.2
40	lime	359	406	89.2	54.0	19.6	11.5	121	64.4
0	20 g kg <sup>-1</sup>	52.0	150	46.6	34.2	11.8	10.4	181	104
10	compost	85.2	234	57.3	33.6	15.3	10.3	131	82.7
20	+ 5 Mg ha <sup>-1</sup>	99.9	176	79.7	44.1	17.0	9.83	130	65.5
40	lime	153	174	79.6	38.7	16.5	14.1	114	67.2
0	20 g kg <sup>-1</sup>	69.8	165	39.6	24.8	12.8	7.41	135	69.7
10	compost	84.4	218	52.3	40.1	15.4	9.13	115	67.2
20	+ 10 Mg ha <sup>-1</sup>	101	1331	79.5	36.9	19.6	9.06	144	67.6
40	lime	134	117	74.3	44.9	17.5	11.0	133	80.1
0	Control	92.5	250	40.7	32.8	11.0	7.65	98.8	58.2
10	(No organic	137	473	55.2	34.2	15.1	8.54	126	79.8
20	matter or	128	333	61.8	27.5	17.2	8.85	123	48.5
40	lime)	192	539	68.6	56.1	20.0	15.9	103	116
Miles (1994)	Adequate	50-300		15-20		6-12		50-70	
	Critical			10-13		5			