The Role of Phytotechnology in the Rehabilitation of the BHPBilliton Cannington Ag-Pb-Zn Mine

Thesis submitted by

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Preface

Significant contributions from the following persons were crucial to the progress of this study. Mr Peter Whitehead and Dr Paul Nelson provided generous support and advice in matter of earth science. Associate Professor Paul Gadek and Dr Peter Franks provided vital access to plant growth facilities. Mr Gary Warren contributed his detailed botanical knowledge of northern Australia. Dr Michael Liddell provided essential laboratory equipment and personnel, namely the technical services of Mr Robert Ennis-Thomas. Dr Michael Steele provided statistical advice for the project. Mr David Godwin provided expertise in experimental design. In addition to funding the project, the Environment Department of the Cannington mine also provided travel and accommodation to and from its operational centres. The Advanced Analytical Centre (AAC) at James Cook University and the Townsville and Brisbane offices of Australian Laboratory Services Ltd provided analytical services for this research project.

The following publications resulting from this research project are currently in press or have been accepted for publication at this time;

Keeling, S.M., 2001, Heavy metal phytoextraction: Turning waste into ore. International Conference on Green Processing 2002. Conference Proceeding of the Australasian Institute of Mining and Metallurgy, p. 137-146

Keeling, S.M. and Werren, G. Phytoremediation: The uptake of metals and metalloids by Rhodes Grass grown on metal contaminated soil. Remediation Journal. In press

Keeling, S.M. Passive uptake of Ag, As, Cd, Pb and Zn by subtropical Australian pasture plant species: implications for the revegetation of metal contaminated soils at mine sites. The Rangeland Journal. Accepted

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This project would not have been possible without the financial support and cooperation of the Environment Department, BHPBilliton Cannington Ag-Pb-Zn Mine, in particular Mr Ross Wilson and Steve Malone. Your support has made it possible for me to fulfil a dream and no amount of beer is going to make up for that. I sincerely hope that these findings, in some small way, help you towards solving land rehabilitation problems that may arise at Cannington.

I also humbly acknowledge receipt of the following grants and awards that made it possible to undertake this research project; (a) James Cook University Earth Science Studentship, (b) Australian Postgraduate Association Industry (APAI) Linkage, (c) Australian Research Council research grant (LP0219428), (d) James Cook University Doctoral Merits Research Scheme and (e) Australasian Institute of Mining and Metallurgy Gold 88 Endowment.

Finally, I thank the friends I have made in Cairns for all the riotous fun, insect repellent and barbequed treats, I shall miss you all very much.

Abstract

Phytotechnology utilises the unique biochemical processes of plants to manage and remediate contaminants such as heavy metals, hydrocarbons, radionuclides and pesticides from soil and water. The use of *in situ* biological systems to rehabilitate large volumes of contaminated soil has enormous potential for application around the globe, particularly in the mining and metal production industries. This study investigated the use of two phytotechnologies (pastoral vegetation covers and chemically-assisted phytoextraction) as environmental tools to manage mine tailings and soil contaminated with mine tailings at the BHPBilliton Cannington Ag-Pb-Zn Mine. The study was conducted in accordance with the mine's Environmental Management Overview System (EMOS) and employed the Australian and New Zealand Environment and Conservation Council (ANZECC) Investigation Guidelines for heavy metal and metalloid contamination of industrial and commercial soil.

Selected pasture plant species (*Chloris gayana*, *Crotalaria novae-hollandiae*, *Cymbopogon ambiguus*, *Cymbopogon bombycinus*, *Cyperus victoriensis*, *Gomphrena canescens* and *Triodia molesta*) were cultivated in soil contaminated with mine tailings (60 μg Ag g^{-1}, 2039 μg As g^{-1}, 30 μg Cd g^{-1}, 11950 μg Pb g^{-1} and 4150 μg Zn g^{-1}). The addition of 5 wt% to 35 wt% mine tailings to uncontaminated soil significantly improved the biomass production of *Chloris gayana*. In contrast, the biomass production of the remaining species (all native pasture plants) was significantly reduced on soil contaminated with 5 wt% to 35 wt% mine tailings. The pasture plant species accumulated low concentrations of heavy metals and metalloids from soil contaminated with mine tailings, indicating their suitability for the revegetation of pastoral lands. In addition, limestone amendments to soil contaminated with mine tailings effectively improved the revegetation potential of *Cymbopogon ambiguus*, *Cymbopogon bombycinus* and *Crotalaria novae-hollandiae* on soil contaminated with mine

tailings, in addition to reducing the uptake of heavy metals and metalloids by the plants.

The chemically-assisted phytoremediation of soil contaminated with mine tailings was investigated using *Chloris gayana*, *Crotalaria novae-hollandiae*, *Cymbopogon bombycinus* and *Cyperus victoriensis* and soil amendments of EDTA, DTPA, EDDS, ammonium thiosulphate, ammonium thiocyanate and thiourea. Plant uptake of heavy metals and metalloids resulting from the application of the soil amendments indicated that, based upon published models for the technology, no pasture plant species would be suitable for the chemically-assisted phytoremediation of contaminated soil at the Cannington mine. *Crotalaria novae-hollandiae* and *Cyperus victoriensis*, however, did tolerate the effects of ongoing soil treatments with EDTA and EDDS, while accumulating modest quantities of heavy metals and metalloids, suggesting that vegetation covers with these plants could be used to phytoremediate low levels of soil contamination.

The leaching of Ag, Pb and Zn from mine tailings using weekly amendments of low-ionic-strength solutions of EDTA, ammonium thiosulphate, ammonium thiocyanate, thiourea and sodium cyanate was investigated over a three-month period. EDTA, ammonium thiosulphate and ammonium thiocyanate leached significant quantities of metals from the mine tailings over an approximate eight-week leaching period. EDTA solutions were found to dissolve large quantities of Pb (28.1%) and Zn (12.6%) from the mine tailings. Zinc dissolution was also high using a solution of ammonium thiosulphate (12.1%) and Ag dissolution was only notable using an ammonium thiocyanate solution (83.7%). The data indicate that chemical leaching of the Cannington mine tailings using low-ionic-strength solutions may remove a large proportion of the wastes contained heavy metals thus increasing metal production at the site, in addition to decontaminating a hazardous mine waste material.

This research project concludes that the pasture plant species investigated are highly suited to the revegetation of soil contaminated with mine tailings. In addition, the study concludes that the native pasture plant species that were deemed appropriate for phytotechnology applications at the Cannington mine are not suitable for the chemically-assisted phytoremediation of soil contaminated with mine tailings. The study also concludes that periodic leaching of the mine tailings using chemical reagents employed for phytoextraction applications has the potential to elevate metal production by reprocessing the waste while also reducing its toxicity and environmental risk.

Glossary of Terms

Chelate: A large molecular weight organic compound, such as EDTA, DTPA and EDDS, having the ability to form soluble complexes with metallic ions (SSSA, 2004).

Chlorinated solvents: Organic solvent containing chlorine atoms, e.g., methylene chloride and 1,1,1-trichloromethane, which are used in aerosol spray containers and in traffic paint (SSSA, 2004).

Ligand: A low molecular weight molecule or ion capable of sharing an electron pair during bonding, such as sulphate (SO_4^{2-}), thiosulphate ($S_2O_3^{2-}$), cyanate (OCN^-) and thiocyanate (SCN^-) (SSSA, 2004).

Metallothioneins (MTs): Low molecular weight proteins and polypeptides involved in the intracellular fixation and regulation of zinc and copper in plants and in neutralising the effects of toxic elements such as cadmium and mercury (SSSA, 2004).

PAHs: Polyaromatic hydrocarbons (SSSA, 2004).

PCB: Polychlorinated biphenyl; a pathogenic and teratogenic industrial compound used as a heat-transfer agent; PCBs may accumulate in human or animal tissue (SSSA, 2004).

Phytochelatin (PCs): Any of a group of plant peptides that bind metals (Cd, Zn, Cu, Pb, Hg) and play important roles in the detoxification of heavy metals (particularly Cd) in plants (BioTech, 2004).

Pyrrolizidine alkaloids: A group of alkaloids characterized by a nitrogen-containing necine, occurring mainly in specimens of the Boraginaceae, Compositeae and Leguminosae plant families (Brown, 2004).

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List of Abbreviations

AAC: Advanced Analytical Centre

AAS: Atomic Adsorption Spectrometry

ALS: Australian Laboratory Services

ANZECC: Australian and New Zealand Environmental Conservation Council

CAP: Chemically-assisted phytoextraction

CDTA: 1,2-Cyclohexanediaminetetraacetic Acid

CEC: Cation exchange capacity

dH_2O: deionised water

DTPA: Diethylenetriaminepentaacetic Acid

DW: Dry weight

E: Dilution factor

EC: Electrical conductivity

EDDS: Ethylenediaminedissuccinatic Acid

EDTA: Ethylenediaminetetraacetic Acid

EGTA: Ethylene Glycol Bis(2-aminoethyl ether)-N,N,N',N'-tetraacetic Acid

EMOS: Environmental Management Overview System

GFAAS: Graphite furnace atomic absorption spectrometry

GXR-3: Geochemical reference material

HEDTA: N-Hydroxyethylenediamine-N,N',N'-tetracetic Acid

HOAc.: Acetic acid

HNO_3: Nitric acid

ICP MS: Inductively coupled plasma mass spectrometry

JCU: James Cook University

LS: Limestone

M: million

NaCN: Sodium cyanide

NH_4HCl: Ammonium hypochlorite

NH_4OAc: Ammonium acetate

NH_4NO_3: Ammonium nitrate

OSM: Osmocote fertiliser

oz: Ounce

P: plant concentration (μg g^{-1})

PGE: Platinum group element

PRF: Process Residue Facility

SCN: Ammonium thiocyanate

ST: Soil-Tailings mixture

STL: Soil-Tailings-Limestone mixture

TEC: Total element concentration

THIO: Thiourea

TPA: Tonnes per annum

TPP: Triphosphate fertiliser

TSP: Ammonium thiosulphate

USEPA: United States Environmental Protection Agency

XRD: X-ray diffraction