

**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.

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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 $\mu\text{g Ag g}^{-1}$, 2039 $\mu\text{g As g}^{-1}$, 30 $\mu\text{g Cd g}^{-1}$, 11950 $\mu\text{g Pb g}^{-1}$ and 4150 $\mu\text{g Zn g}^{-1}$). 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 ($\text{S}_2\text{O}_3^{2-}$), 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
dH₂O:	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
HNO₃:	Nitric acid
ICP MS:	Inductively coupled plasma mass spectrometry
JCU:	James Cook University
LS:	Limestone
M:	million
NaCN:	Sodium cyanide
NH₄HCl:	Ammonium hypochlorite
NH₄OAc:	Ammonium acetate
NH₄NO₃:	Ammonium nitrate
OSM:	Osmocote fertiliser
oz:	Ounce

P:	plant concentration ($\mu\text{g g}^{-1}$)
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