

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

# **Phytoremediation of Mercury-Contaminated Mine Wastes**

A thesis presented in partial fulfilment  
of the requirements for the  
degree of

**Doctor of Philosophy in Soil Science**

**Fábio Netto Moreno**

**Massey University  
Palmerston North  
2004**

## ABSTRACT

Mercury (Hg) is a toxic heavy metal that is concentrated in organisms. Injudicious use of Hg and its compounds have resulted in widespread soil contamination. This study investigates the potential use of plants for the remediation of Hg-contaminated mine wastes. Plants can remove soil Hg via phytoextraction and phytovolatilisation. I investigated both of these strategies by focusing on a methodology for Hg analyses in plants and soils with a view to the determination of volatile Hg emitted from plants. Secondly, I determined the feasibility of Hg phytoextraction and phytovolatilisation from contaminated mine wastes.

An accurate method for the analysis of Hg in air, plant and various soil fractions was a key component of this study. I developed a hydride-generation atomic absorption spectroscopy method for total Hg analyses in digest and liquid matrices of the aforementioned samples. Quality assurance was ensured by comparing results with those of an external certified laboratory. The maximum discrepancy was 15 %.

To measure plant Hg-volatilisation, a method that captures Hg-vapour in solution for subsequent analyses was developed. Initially this system was used to trap Hg vapours released from the root system of *Brassica juncea* plants grown in hydroponic solutions. A subsequent study improved the Hg trapping system, allowing the capture of volatile Hg from both roots and shoots. Mercury recoveries from the whole plant system (traps + plant + solutions) averaged 90 % using this experimental apparatus.

In most contaminated substrates, plant Hg uptake is insignificant, possibly due to the low bioavailability of Hg. This represents an obstacle for effective remediation using phytoextraction. Geochemical studies were carried out in Hg-contaminated substrates to examine the potential of chemical agents to induce Hg solubility and subsequent plant uptake. These studies utilised Hg-contaminated mine tailings collected from three locations: the Tui base-metal mine, in the North Island of New Zealand, the Gold Mountain mine, in North-Central China and, the Serra Pelada artisanal mine site, in Northern Brazil. The results demonstrated that Hg solubility in all tested substrates is increased in the presence of sulphur-containing chemical ligands. The effectiveness of these ligands was influenced by site-specific geochemistry.

Plants species were able to accumulate up to 60 mg/kg of Hg in shoot tissues upon addition of sulphur-containing ligands to Tui and Gold Mountain substrates. The degree of plant-Hg accumulation was shown to be dependant on plant species and on the thioligand-induced soluble Hg fraction. Shoot Hg transport was inhibited for Gold Mountain substrate amended with 1.25g/kg of humic acid. The maximum Hg extraction yield for *B. juncea* plants growing in Tui field sites averaged 25 g per hectare following application of sodium thiosulphate.

Volatilisation of Hg vapour from barren substrates occurred as a result of biotic (microorganisms) and abiotic (chemical and photochemical reduction) processes. The presence of *B. juncea* plants in substrates enhanced the volatilisation process up to 23 fold. Phytovolatilisation was the dominant pathway responsible for between 75 to 99.5 % of the total Hg removed from substrates.

It was concluded that Hg removal from contaminated mine wastes can be accomplished by both thioligand-induced phytoextraction and phytovolatilisation. There are risks of groundwater contamination by Hg species mobilised after application of thioligands to substrates. Estimated Hg (0) emissions from plant-based operations at contaminated sites ranged between 1.5 to 3.6 kg of Hg/ha per year. Due to extensive atmospheric dilution, Hg emissions from small-scale phytoremediation operations would not cause serious harm to the local population or the regional environment. Phytoremediation combined with gold-phytoextraction can help to mitigate Hg-pollution in artisanal mine sites in the developing world.

## **DEDICATION**

I dedicate this thesis to my parents Ivan Netto Moreno and Vilma Reichfeld Netto Moreno who have limitlessly supported my career.

## ACKNOWLEDGEMENTS

First of all, I would to express words of gratitude *in memoriam* of Professor Robert Brooks, whose brilliance in plant metal hyperaccumulation was an incessant source of inspiration for my studies on mercury phytoremediation. I feel privileged to be “supervised” by him during the writing up of my project, when coming to New Zealand for pursuing PhD studies was just a mere possibility. I am sure his intellectual legacy will continue to encourage myself to further work in the field of phytoremediation.

I sincerely thank Bob Stewart for donating time and guidance experience to make my work as much objective and honest as possible. I was also lucky to have Brett Robinson as a supervisor. His research expertise in metal phytoremediation is infallibly precise and I owe the clearness of my work to that. Just upon my arrival in New Zealand, Robert Brooks confessed to me that Chris Anderson would be a good supervisor for my work on Hg. He proved to be right! Chris was not only an attentive supervisor in the lab, in the greenhouse and in the field but also a sensitive adviser during the writing up process. Chris faithfully added to my background his business-related view of phytoremediation and I am grateful for that. We had a great time overseas while collecting tailings samples in the humid Amazonian environment of Serra Pelada or setting up field plots in the dryness areas of Teofilândia (Northern East Brazil) and Bendigo (Southern Australia). I just regret I was not a good partner in drinking beer and “caipirinha” during the time we travelled together!

I acknowledge the financial support of The Centre for Environmental Research in Minerals, Metals and Materials (CERM3) in particular Professor Dr. John A. Meech and Dr. Mory Gomshei for making possible the lab and greenhouse work at the University of British Columbia, in Canada, and the field work at Fazenda Brasileiro gold mine, in Brazil. I am also grateful to A. J. Gunson from the Centre for Responsible Mining at UBC for providing the Hg-contaminated Chinese mine tailings from the Gold Mountain mine. Also sincere thanks to Jennifer Hinton for allowing access to extensive literature on Hg research. To Dr. Marcello Veiga from UBC and to Dr. Villas Bôas from CETEM (Brazil) I acknowledge the time donated on valuable discussions about Hg volatilisation. I am thankful for the support received from my Chilean friend Francisco

A. Melo during lab work at UBC. I also warmly thank the “Big” Family Jara for making my stay in Vancouver so enjoyable.

I express my sincere thanks to Mary Beth Kirkham from Kansas State University, USA, for the valuable comments on Chapters 6 and 8.

I would like to express big thanks to Luciano Ramos, Alcides Paiva, José Cerqueira, and Roberto Nomura from Companhia Vale do Rio Doce (CVRD) for turning into reality the gold field work in Teofilândia and the geological survey in the artisanal mining site of Serra Pelada. Thanks to Dr. Vanessa Torres for allowing access to the mining facilities of CVRD in Belo Horizonte.

I also acknowledge the first-class lab and field assistance provided by Ian Furkert, Bob Toes, Mike Bretherton, Ross Wallace, Glenys Wallace and Anne West from the Earth and Soils Group. Thanks to all the students and the staff, past and present, from the Soil Science Department, the Plant Growth Unit (PGU) and the International Students Office of Massey for keeping me going during the long time of my research work.

I am greatly indebted to the National Council for Technological and Scientific Development (CNPq) from Brazil for fully provided me with the living expenses and the course tuition fees, without which it would have been financially impossible for me to accomplish my PhD studies.

Along these four years in NZ lots of good and not so good things happened in my life. I, therefore, acknowledge the strong support and encouragement from my Family when I most needed. I also say thanks to my girlfriend Momoko Ishii for pulling me up when I was feeling tired and down. I am grateful to Micki Tyler for providing such a peaceful environment for my studies in the flat I rented at 11, Parkland Crescent. My warmest thanks to Patrick Dulin and Rebeca Maseda and to Shawn Stein and Claudia Castillo for generously offering their place for accommodating me and my belongings during the last stage of my thesis.

It was a great source of joy to discover a big Latin American community in Palmerston North, which I am very proud to be part of it. I would like to express my deepest thanks

to the following people: Sylvia Weill, Dora D. Carvalho, Erich Seydewitz and Ignacia Luz, Sabina Jaeger and Raimmond Reuter, Giselle Soares and Matt Perlmutter, Flávio Britto, Dakshina (Moody), Florencia Alliamé, Gonzalo Carracelas and Virginia Porcille, Alan and Carola, Romana Santos, Patrícia Salles, Wagner and Angela, Vasco, Alejandra Ayanegualcerreca, Klelia, Victor, Christian and Paulina, Juan Carlos and Patricia, Paulina Moreno, Paulina Hussein, Pépe Barquíz, Tyne and Amanda, Rogério, Steve and Gloria Anne, Dewin, Lyn James, Romana Santos, Ana Paula and Rick, Daniela and Stuart, Ximenita, Walter and Kika, Constantino, Paulo Viteritte, Tyn, Antonius Tri, Arivin, Saman, Jagretti, Rita, Asoka, Edmundo. Special thanks to the Family Ishii for making my stay in Japan so enjoyable.

A great deal of inner strength I acquired through solid Yoga teachings provided by Ruth Hogson, Frank Sligo, Michael Jones and Bevan-“ananda”.

To the plants species I tested in my research I acknowledge their noble sacrifice in the name of Science.

*“The most beautiful thing  
we can experience is the  
Mysterious. It is the source  
of all true art and science”.*

*ALBERT EINSTEIN (1879-1955)*

**TABLE OF CONTENTS**

<b>ABSTRACT</b> .....	i
<b>DEDICATION</b> .....	iii
<b>ACKNOWLEDGEMENTS</b> .....	iv
<b>TABLE OF CONTENTS</b> .....	viii
<b>LIST OF FIGURES</b> .....	xii
<b>LIST OF TABLES</b> .....	xiv
<b>CHAPTER 1- INTRODUCTION</b> .....	1
1.1 Statement of the problem .....	1
1.2 Aims of the study .....	2
1.3 Structure of the thesis .....	2
References .....	3
<b>CHAPTER 2 - LITERATURE REVIEW</b> .....	4
2.1 Mercury and its uses .....	4
2.1.1 Artisanal and small-scale mining .....	4
2.2 Mercury in the Environment .....	6
2.2.1 Anthropogenic sources .....	6
2.2.2. Natural sources .....	7
2.3 Mercury in Plants .....	8
2.3.1 A brief historical background .....	8
2.3.2 Toxicity and tolerance .....	10
2.3.3 Mobilisation .....	11
2.3.4 Uptake and transport .....	13
2.3.5 Volatilisation .....	14
2.4 Mercury in Soils .....	16
2.4.1 Speciation of soluble Hg in the soil .....	16
2.4.2 Retention of Hg in the soil .....	17
2.4.3 Mobility and transport of Hg .....	18
2.5 Mercury Pollution and Remediation .....	19
2.5.1 Pollution .....	19
2.5.2 Remediation .....	21
2.6 Phytoremediation .....	22
2.6.1 Definition .....	22
2.6.2 Phytovolatilisation .....	23
2.6.2 Phytoextraction .....	25
References .....	28
<b>SECTION A - METHODOLOGICAL APPROACH FOR THE ANALYSES OF MERCURY IN PLANTS AND SOILS AND FOR THE MEASUREMENT OF VOLATILE MERCURY EMITTED FROM PLANTS</b> .....	38
<b>CHAPTER 3 - MERCURY ANALYSIS OF PLANT AND SOIL SAMPLES USING THE HYDRIDE-GENERATION AAS METHOD</b> .....	39
Abstract .....	39
3.1 Introduction .....	40
3.2 Material and Methods .....	41

3.2.1 Standards and reagents .....	41
3.2.2 Mercury-rich plant samples.....	41
3.2.3 Extraction procedures.....	42
3.2.3.1 Substrate samples .....	42
3.2.3.2 Plant samples.....	42
3.2.4 Reproducibility of the method .....	42
3.2.5 Quality control assessment.....	43
3.2.6 Instrumentation .....	43
3.3 Results and Discussion.....	44
3.3.1 Formation of Hg <sup>0</sup> .....	44
3.3.2. System calibration.....	45
3.3.3 System reproducibility .....	46
3.3.4 Quality control assessment.....	47
3.4 Conclusions .....	50
References .....	50

**CHAPTER 4 - IS VOLATILISATION A SIGNIFICANT PROCESS FOR MERCURY PHYTOREMEDIATION? .....** 52

Abstract .....	52
4.1 Introduction .....	53
4.2 Material and Methods .....	54
4.2.1 Plant growth conditions .....	54
4.2.2 Collection of volatile Hg.....	54
4.2.3 Plant analysis.....	56
4.2.4 Mercury analysis .....	56
4.2.5 Mass balance calculations.....	56
4.3 Results .....	57
4.4 Discussion .....	60
4.5 Conclusions .....	61
References .....	61

**CHAPTER 5 - MEASURING VOLATILE MERCURY RELEASED FROM PLANTS .....** 63

Abstract .....	63
5.1 Introduction .....	64
5.2 Material and Methods .....	65
5.2.1. Plant growth conditions.....	65
5.2.2 Collection of volatile Hg.....	66
5.2.3 Plant analysis.....	68
5.2.4 Mercury analysis .....	68
5.3 Results and Discussion.....	68
5.5 Conclusions .....	72
References .....	72

**SECTION B - THE PHYTOEXTRACTION AND PHYTOVOLATILISATION OF MERCURY FROM CONTAMINATED MINE WASTES..... 75**

**CHAPTER 6 - INDUCED PLANT UPTAKE AND TRANSPORT OF MERCURY IN THE PRESENCE OF SULPHUR-CONTAINING LIGANDS AND HUMIC**

<b>ACID .....</b>	<b>77</b>
Abstract .....	77
6.1 Introduction.....	77
6.2 Material and Methods .....	79
6.2.1 Site description.....	79
6.2.2 Substrate preparation.....	80
6.2.3 Extractable Hg.....	80
6.2.4 Induced plant-Hg accumulation experiments.....	81
6.2.4.1 Effect of plant species x sulphur-containing ligands .....	81
6.2.4.2 Effect of substrate Hg concentrations and humic acid levels .....	81
6.2.5 Plant harvest .....	82
6.2.6 Plant digestion.....	82
6.2.7 Substrate digestion .....	82
6.2.8 Mercury Analysis .....	83
6.2.9 Statistical analysis .....	84
6.3 Results.....	84
6.3.1 Total and extractable-Hg concentrations .....	84
6.3.2 Effect of plant species x sulphur-containing ligands .....	87
6.3.3 Effect of substrate Hg concentrations and humic acids levels .....	89
6.4 Discussion .....	94
6.4.1. Mercury speciation in the substrate.....	94
6.4.2 Root Hg accumulation in relation to plant species .....	95
6.4.3 Selectivity of mercury complexes to shoot transport.....	95
6.4.4 Effect of humic acids on root uptake .....	96
6.5 Conclusions .....	97
References .....	98

**CHAPTER 7 - PHYTOREMEDIATION OF MERCURY-CONTAMINATED MINE TAILINGS BY INDUCED PLANT-Hg ACCUMULATION ..... 101**

Abstract .....	101
7.1 Introduction .....	101
7.2 Material and Methods .....	104
7.2.1 Site description.....	104
7.2.2 Substrate characterization .....	104
7.2.3 Extractable Hg.....	106
7.2.4 Soluble Hg plant accumulation .....	106
7.2.5 Induced plant-Hg accumulation .....	106
7.2.6 Plant harvest .....	107
7.2.7 Plant digestion.....	108
7.2.8 Soil digestion.....	108
7.2.9 Mercury analyses .....	108
7.2.10 Statistical analysis .....	109
7.3 Results.....	109
7.3.1 Total and chemically solubilised Hg.....	109
7.3.2 Soluble Hg plant accumulation .....	111

7.3.3 Induced plant-Hg accumulation.....	113
7.4 Discussion .....	117
7.5 Conclusions.....	120
References.....	120

**CHAPTER 8 - MERCURY VOLATILISATION AND PHYTOEXTRACTION FROM BASE-METAL MINE TAILINGS.....**

Abstract .....	124
8.1 Introduction .....	124
8.2 Material and Methods .....	126
8.2.1 Substrate characterization .....	126
8.2.2 Plant growth conditions .....	126
8.2.3 Extractable Hg.....	127
8.2.4 Effect of ammonium thiosulphate on Hg volatilisation.....	127
8.2.5 Effect of ammonium thiosulphate levels on plant-Hg accumulation.....	128
8.2.6 Induced Plant-Hg Accumulation Field Trials .....	129
8.2.7 Plant harvest.....	129
8.2.8 Plant digestion.....	129
8.2.9 Substrate digestion .....	130
8.2.10 Mercury analysis .....	130
8.2.11 Statistical analysis .....	131
8.3 Results and Discussion.....	131
8.3.1 Volatilisation and induced plant-Hg accumulation pot trials.....	131
8.3.2 Induced plant-Hg accumulation field trials.....	135
8.3.3 Considerations about the environmental impacts .....	140
8.4 Conclusions.....	143
References.....	144

**CHAPTER 9 - MERCURY PHYTOEXTRACTION AND PHYTOVOLATILISATION FROM Hg-CONTAMINATED ARTISANAL MINE SITES.....**

Abstract .....	147
9.1 Introduction.....	148
9.2 Material and Methods .....	150
9.2.1 Substrate type .....	150
9.2.3 Substrate preparation for plant growth.....	152
9.4 Extractable Hg.....	153
9.5 Plant-Hg volatilisation and accumulation experiments.....	153
9.6 Plant harvest.....	154
9.7 Plant digestion.....	155
9.8 Substrate digestion .....	155
9.9 Mercury analysis .....	155
9.10 Statistical analyses .....	156
9.3 Results .....	157
9.3.1 Total and extractable Hg in substrates .....	157
9.3.2 Effect of plants, substrate type and sulphur-containing ligands .....	158
3.3 Soil-plant trends in the Hg volatilisation from planted substrates .....	160
9.4. Discussion .....	164
9.4.1 Speciation and solution geochemistry of Hg complexes .....	164
9.4.2 Origin and possible role of plant-Hg emissions .....	166
9.4.3 Implications for the Hg phytoremediation .....	168

9.4.4 Gold phytoextraction as a strategy for Hg remediation .....	171
9.5 Conclusions.....	172
References.....	173
<b>CHAPTER 10 - CONCLUSIONS .....</b>	<b>178</b>
10.1 Conclusions and implications from this study .....	178
10.2 The future of Hg-phytoextraction .....	186
10.3 Concluding remarks .....	187
<b>APPENDICES .....</b>	<b>187</b>
Appendix 1: Gold phytoextraction field trials .....	187
Appendix 2: Plant References.....	196
Appendix 3 : Thesis Data Set.....	197

## LIST OF FIGURES

### CHAPTER 2

<b>Figure 2.1.</b> Artisanal gold mine site in the Brazilian Amazon.....	5
<b>Figure 2.2.</b> Direct open-air burning of the amalgam. ....	6
<b>Figure 2.3.</b> Schematic view of iron ferric mobilization by phytosiderophore excretion, rhizosphere acidification and plasma membrane bound metal reductases. ....	12
<b>Figure 2.4.</b> Schematic cross-section of a primary root. ....	14
<b>Figure 2.5.</b> The mercury biogeochemical cycle.....	20
<b>Figure 2.6.</b> View of a metal-tolerant flora dominated by <i>Thlaspi caerulescens</i> over the base-metal mine waste of the Les Malines mining area (France).....	26
<b>Figure 2.7.</b> Phytoremediation of Ni-contaminated soils in Rustenburg, South Africa (A). The Ni-hyperaccumulator <i>Berkheya coddii</i> (B) was grown at a site near the refining facilities of the Anglo American Platinum Corporation (AMPLATS). Nickel ingots were recovered after harvesting and processing the Ni-rich plant biomass (C). ....	26

### CHAPTER 3

<b>Figure 3.1.</b> Schematic diagram of the hydride generation apparatus. ....	43
<b>Figure 3.2.</b> Calibration graph for the hydride-generation method. ....	45
<b>Figure 3.3.</b> Relative peak heights for Hg concentrations as a function of the sample volume added to the reaction vessel.....	47
<b>Figure 3.4.</b> Comparison of the ability of 2 solutions to extract Hg from a tailings reference substrate containing 100 mg/kg of Hg. ....	48
<b>Figure 3.5.</b> Relative peak heights in Hg-rich plant samples as a function of volume of sample added to the reaction vessel. ....	49

### CHAPTER 4

<b>Figure 4.1.</b> Experimental apparatus used for trapping volatile Hg released from <i>B. juncea</i> roots. ....	55
<b>Figure 4.2.</b> The experimental apparatus inside the temperature-controlled chamber. ...	55
<b>Figure 4.3.</b> Hg mass ( $\mu\text{g}$ ) volatilised from roots of hydroponically grown <i>B. juncea</i> . ..	57
<b>Figure 4.4.</b> Relationship between Hg volatilisation (mg of Hg per kg of dry weight roots) and root Hg accumulation (mg/kg dry weight) by <i>B. juncea</i> plants. ....	58

<b>Figure 4.5.</b> Comparison between Hg volatilisation from shoots (estimated) and roots (mg/kg dry weight). .....	59
<b>Figure 4.6.</b> Normalized (100%) mass values for Hg accumulated in the plant, remained in solution and volatilised to the air for <i>B. juncea</i> . grown in nutrient solution and treated with soluble Hg (HgCl <sub>2</sub> ). .....	59
<b>CHAPTER 5</b>	
<b>Figure 5.1</b> Experimental unit used for trapping Hg from roots and shoots of <i>B. juncea</i> . .....	67
<b>Figure 5.2.</b> View of the experimental apparatus inside the controlled environment cabinet. ....	67
<b>Figure 5.3.</b> Total Hg mass (µg) volatilised from <i>B. juncea</i> plants and controls (no plants). .....	69
<b>Figure 5.4.</b> Volatilisation of Hg by shoots and roots of <i>B. juncea</i> plants. Values are expressed on (A) mass (µg) and (B) concentration (mg/kg dry weight). .....	70
<b>Figure 5.5.</b> Mass balance for the Hg distribution between the air, plant and solution compartments. ....	71
<b>CHAPTER 6</b>	
<b>Figure 6.1.</b> Pots with <i>B. juncea</i> plants inside the greenhouse. ....	83
<b>Figure 6.2.</b> Effect of sulphur-containing ligands on extractable Hg concentrations of original Gold Mountain mine tailings. ....	86
<b>Figure 6.3.</b> Humic acid-extractable Hg for modified substrates containing Hg at 2.5 mg/kg. ..	86
<b>Figure 6.4.</b> Accumulation of Hg in roots and shoots of (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> -treated <i>B. juncea</i> plants as a function of total (a) and NH <sub>4</sub> S <sub>2</sub> O <sub>3</sub> -extractable (b) Hg concentrations in modified substrates. ....	90
<b>Figure 6.5.</b> Accumulation of Hg in roots of water and (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> -treated <i>B. juncea</i> plants as a function of the humic acid content (g/kg) in modified substrates containing Hg at 2.5 mg/kg. ....	91
<b>Figure 6.6.</b> Accumulation of Hg in shoots of (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> -treated <i>B. juncea</i> plants as a function of the humic acid content (g/kg) in modified substrates containing Hg at 2.5 mg/kg. ....	92
<b>Figure 6.7.</b> Accumulation of Hg in roots (a) and shoots (b) of control and (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> -treated <i>B. juncea</i> plants as a function of extractable Hg in humic acid amended substrates (1.25 g/kg) containing Hg at 2.5 mg/kg. ....	93
<b>CHAPTER 7</b>	
<b>Figure 7.1.</b> Location of Tui mine tailings. The tailings dam is located on the NW flank on Mount Te Aroha, approximately 3 km of the township of Te Aroha, North Island of New Zealand (A). Revegetation trials ongoing in the Tui mine tailings (B). ....	105
<b>Figure 7.2.</b> Total Hg concentrations for the 12 locations sampled along the Tui mine tailings. ....	109
<b>Figure 7.3.</b> Chemically solubilised Hg as a function of S-containing ligands applied to Tui mine tailings at a 2g/L concentration, (except H <sub>2</sub> O <sub>2</sub> , [0.27%]). ....	110
<b>Figure 7.4.</b> Chemically solubilised Hg as a function of ammonium thiosulphate applied to Tui mine tailings at the concentrations of 0, 1 and 10g/L. ....	111
<b>Figure 7.5.</b> Accumulation of Hg in roots (A) and shoots (B) of <i>Atriplex canescens</i> and <i>Berkheya coddii</i> grown in Tui mine tailings treated with 1, 5, and 10mg/kg of soluble Hg (HgCl <sub>2</sub> ). ..	112

<b>Figure 7.6.</b> Total Hg concentrations in controls and planted substrates after application of 1, 5 and 10mg/kg of soluble Hg ( $\text{HgCl}_2$ ) to pots. ....	113
<b>Figure 7.7.</b> Shoot Hg concentrations of <i>Brassica juncea</i> and <i>Lupinus</i> sp. after application of S-containing ligands at 2g/kg to Tui mine tailings. ....	114
<b>Figure 7.8.</b> Hg concentrations in leachates collected from <i>Brassica juncea</i> and <i>Lupinus</i> sp. pots after application of S-containing ligands at 2g/kg to Tui mine tailings. ....	115
<b>Figure 7.9.</b> Normalised (100%) values of plant, soil, leachates and unaccounted Hg from <i>Brassica juncea</i> and <i>Lupinus</i> sp. after application of ammonium thiosulphate at 2g/kg to Tui mine tailings. ....	116

## CHAPTER 8

<b>Figure 8.1.</b> Experimental unit used for trapping Hg released from plants. ....	128
<b>Figure 8.2.</b> Volatilisation rates from <i>B. juncea</i> plants grown in Tui mine tailings treated with ammonium thiosulphate ( $[\text{NH}_4]_2\text{S}_2\text{O}_3$ ) at 1 g/Kg. (A) Total Hg mass ( $\mu\text{g}/\text{day}$ ) emitted from plants and control pots (without plants) and (B) Total Hg mass emitted from plants per unit dry weight (kg) per day. ....	131
<b>Figure 8.3.</b> Root (A) and shoot (B) Hg concentrations of <i>B. juncea</i> plants after addition of ammonium thiosulphate ( $[\text{NH}_4]_2\text{S}_2\text{O}_3$ ) at 1 g/kg to Tui mine tailings. ....	132
<b>Figure 8.4.</b> Total (A) and extractable (B) Hg concentrations in Tui mine tailings after growth of <i>B. juncea</i> plants and application of ammonium thiosulphate ( $[\text{NH}_4]_2\text{S}_2\text{O}_3$ ) at 1 g/kg. ....	133
<b>Figure 8.5.</b> Mercury Distribution in the air-plant-soil system after application of ammonium thiosulphate ( $[\text{NH}_4]_2\text{S}_2\text{O}_3$ ) at 1 g/kg to Tui mine tailings. Normalized values (100 %) represent the Hg mass in substrate, plant and acid trap (A) and the Hg mass partition between root, shoot and trap compartments (B). ....	134
<b>Figure 8.6.</b> Root (A) and shoot (B) Hg concentrations of <i>B. juncea</i> plants after addition of increasing concentrations of ammonium thiosulphate ( $[\text{NH}_4]_2\text{S}_2\text{O}_3$ ) to Tui mine tailings. ....	135
<b>Figure 8.7.</b> Extractable Hg concentrations as a result of sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) application to Tui mine tailings at concentrations of 2 and 10 g/L. Bars denote $\pm 1$ standard deviation from the mean of 3 replicates. Note that (*) means Hg below detection levels. ....	136
<b>Figure 8.8.</b> Experimental field plot at the Tui mine tailings (North Island, NZ) before application of sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) to the substrate. ....	137

## CHAPTER 9

<b>Figure 9.1.</b> Location of the Serra Pelada artisanal mine site. ....	151
<b>Figure 9.2.</b> View of a tailings area within the artisanal gold mine site of Serra Pelada (June 2003). ....	152
<b>Figure 9.3.</b> Effect of sulphur-containing ligands (applied at 2 g/kg substrate) and <i>aqua regia</i> on extractable Hg concentrations of Serra Pelada (SP) and Gold Mountain (GM) substrates. ....	157
<b>Figure 9.4.</b> Whole plant-Hg concentrations in <i>B. juncea</i> after application of sulphur-containing ligands at 2 g/kg to Gold Mountain (a) and Serra Pelada (b) substrates. ....	160
<b>Figure 9.5.</b> Total (a) and extractable (b) Hg concentrations in Gold Mountain substrates after growth of <i>B. juncea</i> plants and application of ammonium thiosulphate ( $[\text{NH}_4]_2\text{S}_2\text{O}_3$ ) at 2 g/kg. ....	160
<b>Figure 9.6.</b> Mercury distribution in the air-plant-soil system after application of ammonium thiosulphate ( $[\text{NH}_4]_2\text{S}_2\text{O}_3$ ) at 2 g/kg to Gold Mountain substrates. ....	161

**Figure 9.7.** Mercury mass partition between root, shoot and trap compartments after application of ammonium thiosulphate ( $[\text{NH}_4]_2\text{S}_2\text{O}_3$ ) at 2 g/kg to Gold Mountain substrates. .... 162

**Figure 9.8.** Volatile Hg mass ( $\mu\text{g}$ ) emitted from *B. juncea* plants as a function of the Hg concentration in plant tissues (mg/kg DW). .... 163

**Figure 9.9.** Volatile Hg mass ( $\mu\text{g}$ ) emitted from *B. juncea* plants as a function of the Hg concentration in the substrates (mg/kg). .... 164

**Figure 9.10.** Eh-pH diagram for part of the system Hg-O-H-S-Cl. . .... 165

**CHAPTER 10**

**Figure 10.1.** Proposed strategy for the remediation of Hg-contaminated soils in artisanal mine sites. .... 185

**LIST OF TABLES**

**CHAPTER 3**

**Table 3.1.** Determination of  $\text{Hg}^{2+}$  in deionized water samples. ....46

**Table 3.2.** Comparative analysis between the hydride generation and ICP-MS methods for the Hg determination in Hg-spiked solutions and Hg-rich plant samples. .... 49

**CHAPTER 6**

**Table 6.1.** Mercury concentrations and the pH and Eh of original and modified samples of Gold Mountain (GM) mine tailings. .... 85

**Table 6.2.** Effect of sulphur-containing ligands and plant species on plant-Hg accumulation for plants growing in modified substrates. ....87

**Table 6.3.** Linear contrasts and the associated F-ratio and *p*-values for the comparison of plant/chemical treatment means. ....88

**CHAPTER 7**

**Table 7.1.** Dry matter yield (g/pot) of *Berkheya coddii* and *Atriplex canescens* in Tui mine tailings treated with 1, 5 and 10 mg/kg of soluble Hg ( $\text{HgCl}_2$ ). ....112

**Table 7.2.** Root Hg concentrations (mg/kg) of *Brassica juncea* and *Lupinus* sp. after application S-containing ligands at 2 g/kg to Tui mine tailings. .... 114

**CHAPTER 8**

**Table 8.1.** Phytoextraction results for the Tui mine tailings after application of sodium thiosulphate ( $\text{Na}_2 \text{S}_2\text{O}_3$ ) at 5 g/kg (unless otherwise stated) to Tui tailings field plots.136

**CHAPTER 9**

**Table 9.1.** Selected geochemical characteristics of the Serra Pelada (SP) and Gold Mountain (GM) mine tailings. ....150

**Table 9.2.** Mercury mass ( $\mu\text{g}$ ) volatilised from planted and unplanted Serra Pelada (SP) and Gold Mountain (GM) substrates. ....158

**Table 9.3.** Linear contrasts and the associated F-ratio and *p*-values for the effect of *B. juncea* plants, sulphur-containing ligands and substrate type on volatile Hg emissions from Serra Pelada (SP) and Gold Mountain (GM) substrates. ....159