

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.

This thesis is presented in partial fulfillment of the requirements for
the degree of Master in Science

Cher LaCoste BSc. Env.

January, 2000

Errata

Contents pages: Numbering out by one unit after page 14 which should be page 13. All subsequent pages should be one less. Hence also Table 4 is on page 30 not 31.

Page 2 line 6: "its" not "it's".

Page 12: last sentence should read "The permissible values may be different for various countries or states depending on individual regulation and land use."

Page 20 line 6: the part of the equation that shows " π^2/mc " should read as " π^2e^2/mc ".

References:

Page 19: "Patel and Agarwal 1991" should read as "Patel and Agarwal 1992".

"Cleven and Fokkert 1994" should read as "Cleven and Fokkert 1993".

Page 36 line 14: "Stockey" should read as "Stockley".

Page 61: Nicks and Chambers reference: "phytominig" should read as "phytomining".

Page 63 at top: The Stockley (1980) ref. is missing and should read as follows:

Stockley, E. 1980. Biogeochemical Studies on the Nickel Complex Contained in the Nickel-accumulating Legume *Pearsonia metallifera* from the Great Dyke Area, Zimbabwe. BSc (Hons.) Thesis, Massey University, Palmerston North, New Zealand.

Page 63 line 3: The date of the Tremel et al. ref. is 1997 not 1996.

Acknowledgements: I would like to thank my supervisors Dr. Robert Brooks, Dr. Brett Robinson, use of the facilities and the assistance of the faculty of Soil and Earth Science Department, Massey University.

Thanks are also extended to the Delmot family for their seed collection and A. Chiarucci for his assistance. Thank you to the University of Montpellier for allowing use of it's analytical services. Scholarship funding was provided for by Antrim Forest Products Ltd.

Thallium Phytoextraction and its Economic Significance

LIST OF FIGURES.....	5
LIST OF TABLES.....	6
ABSTRACT.....	7
CHAPTER 1: GENERAL INTRODUCTION	9
DISCOVERY AND GENERAL PROPERTIES OF THALLIUM	9
SOURCES OF POLLUTION AND GEOCHEMISTRY OF THALLIUM	9
USES.....	10
TOXICOLOGY	11
<i>Animals</i>	11
<i>Plants</i>	11
<i>Micro-organisms</i>	12
REGULATION OF THALLIUM IN THE ENVIRONMENT.....	12
THALLIUM ACCUMULATION BY PLANTS.....	14
PHYTOREMEDIATION	16
PHYTOMINING.....	17
AIMS OF STUDY.....	18
CHAPTER 2: DEVELOPMENT OF A METHOD FOR THALLIUM QUANTIFICATION USING GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY	19
ABSTRACT	19
INTRODUCTION	19
<i>Analytical Techniques Available</i>	20
<i>Analytical Techniques Chosen</i>	20
MATERIALS AND METHODS	22
RESULTS AND DISCUSSION.....	22
CONCLUSIONS.....	24
CHAPTER 3: THALLIUM ACCUMULATION BY <i>IBERIS</i> AND <i>BISCUTELLA</i> SPECIES AND THE POTENTIAL FOR THALLIUM PHYTOEXTRACTION.....	25
ABSTRACT	25
INTRODUCTION	25
MATERIALS AND METHODS.....	27
<i>Site descriptions</i>	27
<i>Sample collection</i>	27
<i>Plant digestion</i>	28
<i>Soil digestion</i>	30
<i>Estimation of the pH and plant-available elemental fractions in the soils and mine waste</i>	30
<i>Chemical analysis</i>	30

RESULTS AND DISCUSSION	30
<i>Accumulation of metals by Iberis intermedia and Biscutella laevigata</i>	30
<i>Relationships between plant-metal concentrations and soil properties for Biscutella laevigata</i>	32
<i>The relationship between extractable and total thallium concentrations in soils</i>	33
<i>The potential use of B. laevigata and I. intermedia for phytoremediation/phytomining of thallium-rich soils</i>	34
CONCLUSIONS.....	35
CHAPTER 4: SEQUENTIAL EXTRACTION OF THALLIUM FROM <i>IBERIS INTERMEDIA</i> AND <i>BISCUTELLA LAEVIGATA</i>	36
ABSTRACT	31
INTRODUCTION	36
MATERIALS AND METHODS	37
RESULTS AND DISCUSSION.....	38
CONCLUSIONS.....	39
CHAPTER 5: UPTAKE OF THALLIUM BY VEGETABLES: ITS SIGNIFICANCE FOR HUMAN HEALTH, PHYTOREMEDIATION AND PHYTOMINING	40
ABSTRACT	40
INTRODUCTION	41
MATERIALS AND METHODS.....	42
RESULTS AND DISCUSSION	44
<i>Experimental data</i>	45
<i>Health hazards of ingestion of thallium-rich vegetables</i>	56
<i>Phytoremediation of thallium-contaminated soils</i>	57
<i>Phytomining for thallium</i>	58
CONCLUSIONS.....	59
CHAPTER 6: SUMMARISING CONCLUSIONS	60
REFERENCES	61

List of Figures

FIGURE 1: Absorbance curve of standard thallium solutions mg/L.....	22
FIGURE 2: Absorbance peak for 1mg/L thallium solution.....	22
FIGURE 3: Location maps of collection sites for Iberis and Biscutella in a) France b) Italy.....	27
FIGURE 4: Uptake of thallium by Biscutella as a function of the extractable (1M ammonium acetate) Tl concentration in the soil.	31
FIGURE 5: Percentage of the total metal concentration in soil that is extractable with 1M ammonium acetate.	32
FIGURE 6: Concentrations of soil absorbed Tl from solution.	42
FIGURE 7: Thallium concentrations of vegetables and Iberis when grown in loam treated with 0.7mg/kg and 3.7mg/kg.	52
FIGURE 8: Bean leaf showing chlorosis along the veins typical of thallium toxicity	45
FIGURE 9: Bean plant before harvest. Control plant appears normal and healthy, chlorosis seen in the high treatment of 3.7mg/kg.	45
FIGURE 10: All three beetroot plants look normal and healthy with a slight decrease in biomass with increasing thallium concentrations.	46
FIGURE 11: Control and low treatment of cabbage are normal and healthy. Highest treatment caused slight yellowing but difference in height is observed.	46
FIGURE 12: Iberis plant in bloom in 3.7mg/kg of thallium which has no effect on germination or growth.	47
FIGURE 13: Lettuce growth appeared normal even when treated with thallium.	48
FIGURE 14: Onion shown one week prior to harvest. Thallium treatments caused slower germination and decreased biomass.	48
FIGURE 15: Pea plants shown; control and treatment one exhibited normal growth. Treatment two plants were yellow at the bottom and the tendrils were not responsive. ..	49
FIGURE 16: Spinach plants treated with 0.7ppm Tl and the control were normal and healthy. The highest treatment showed no effects other than less new shoot growth. ...	49

FIGURE 17a:Radish control and two thallium treatments shown. Leaf growth appears normal.50

FIGURE 17 b,c,d (from left to right): Close up of radish root. The control is a normally developed pear shape root. Radish grown in 0.7mg/kg (b) and 3.7mg/kg (c) exhibits a long tube formation possibly indicating hormonal disruption due to Tl.50

FIGURE 18: Tomato plants with no visible difference between treatments.51

FIGURE 19: Turnip plants; highest treatment poor growth of leaves and root and chlorosis.51

FIGURE 20: Watercress was slightly inhibited at the first Tl level, no survival at 3.7mg/kg.51

List of Tables

TABLE 1: Permitted concentrations (mg/kg) of Tl in soils.13

TABLE 2: Parameters used for the quantification of Tl by GFAAS.21

TABLE 3: Mean (geometric) elemental concentrations (mg/kg-dry mass) in *Iberis intermedia* and *Biscutella laevigata* from St. Laurent le Minier (France) and Rocca San Silvestro (Italy).29

TABLE 4: Correlation matrix for heavy metals in plants and associated soils for *Biscutella* from metal contaminated soils at St. Laurent le Minier, southern France.31

TABLE 5: Concentrations of Tl in sequential extracts according to the Bowen method.36

TABLE 6: Species and cultivars used in experiments.41

TABLE 7: Maximum values of biological absorption coefficients (BAC) for thallium in plant.43

TABLE 8: Effect on biomass of vegetables after various thallium treatments.52

Abstract

Thallium is a volatile toxic metal which has many industrial uses. The sources of thallium include natural geochemical sources and by-products of industrial processes. One of the problems in assessing thallium pollution potential is the lack of an accurate method of quantification of this element. Flame atomic absorption spectrometry (FAAS) is a good method of analysis but only down to the 1.0 mg/kg (ppm) level. For lower concentrations, analytical techniques have been difficult and inaccurate. A newly described method using graphite furnace atomic absorption spectrometry (GFAAS) has been found useful for low Tl concentrations. A method was designed to detect low concentrations of thallium in plant and soil samples. The graphite furnace technique worked well for the data presented in this paper. However, samples of different origin could have more severe matrix effects such as high iron contents.

Thallium has been found to be readily available for plant uptake. The extractability of thallium was significantly higher than other metals such as cadmium and zinc. This property is ideal when considering a possible phytoextraction operation. Two plant species were found to accumulate thallium to levels up to 411mg/kg in *Iberis intermedia* and 504mg/kg in *Biscutella laevigata*. These high values indicate potential for phytoremediation and phytomining in areas of sufficient contamination. The properties of which make thallium an ideal candidate for phytoremediation also make the metal a high risk for biota.

Experiments were also conducted to determine the partitioning and sequestration of thallium within plant organelles. This work was limited to the two hyperaccumulating species but future work could compare non-tolerant species. Evidence from this research might give a better understanding to the mechanism involved in plant uptake and storage of thallium. Agricultural crops used for human consumption or animal grazing may cause deleterious health effects. Thallium is extremely toxic, affecting the nervous system and impairing heart function at low levels. Higher concentrations will cause death. It is possible that some of the illness symptoms observed in humans may be derived from low levels of

thallium in foodstuffs. Aside from a few economic mineral deposits, there is no information of a world-wide distribution of thallium, so health effects can not be accurately assessed.

This thesis describes experiments carried out on common vegetable and their uptake of thallium to determine safe levels of this element within the soil. This information will also be useful to farmers growing crops on contaminated soil will advise them on which plants would uptake less thallium. Thallium has not been studied as extensively as many other heavy metals that are more common in the environment. Although the crustal abundance of thallium is low (0.49-0.7 mg/kg average range), the toxicity of this element is very high, and it is readily available for plant uptake. The toxic effects on animals and plants should be monitored closely.