ENVIRONMENTAL IMPLICATIONS OF PHYTOEXTRACTION FOR MERCURY AND GOLD

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ABSTRACT

The overall objective of this study was to investigate how plants could be used to harvest gold (phytomining) and at the same time remove mercury (phytoremediation) from auriferous mercury-contaminated soils. This study was undertaken to find appropriate plants that could be used to harvest gold, residual in mine tailings or in uneconomic low-grade ore, and at the same time remove residual mercury, commonly used to extract the gold in artisanal mining areas. Different procedures involving analytical methodology, leaching of acid mine tailings and the growing of plants in both gold and mercury-bearing substrates were undertaken.

The analytical methods involved in the analysis of gold in the laboratory using the modern instruments were Flame Atomic Absorption Spectrometry (FAAS) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS). The determination of mercury involved using Flameless Atomic Absorption Spectrometry.

To understand the induced solubility of metals in phytoextraction, Tui mine tailings were leached with several chemicals known to solubilise gold: ammonium thiocyanate, ammonium thiosulphate and urea. The pH of the tailings material was varied through amendment with lime to examine the effect of this geochemical parameter on metal solubility and thus the potential for both plant uptake and leaching. The Tui mine tailings were chosen because of their geochemistry; these are highly weathered sulphide-ore tailings that leach heavy metals into adjacent water systems.

The induced-phytoextraction potential of root crops was also examined in this thesis. Five root crops were grown in an artificial substrate consisting of 3.8 mg/kg (ppm) of elemental gold dispersed in sand. The possibility of using these root crops for phytomining was determined by separately adding chelating agents ammonium thiocyanate and ammonium thiosulphate to the substrate. In most cases there was a higher gold concentration in the roots than in the shoots. The highest mean gold

concentrations were found in carrot roots and in roots of two radish cultivars. It was concluded that there was some potential for the use of carrot to grow an economic crop of gold from mine tailings.

Results obtained from experiments where plants were grown in Tui tailings indicated that both chicory and *Brassica juncea* could be used for the phytoextraction of gold and mercury in the same crop. Under acidic conditions thiocyanate induced the uptake of gold by *Brassica juncea* and the uptake of mercury by chicory; and thiosulphate induced the uptake of mercury by chicory, but it did not induce the uptake of gold by the same plant. Under alkaline conditions, treatment with ammonium thiosulphate induced the uptake of gold and mercury by *Brassica juncea;* and treatment with thiosulphate induced the uptake of mercury by chicory but it did not induce the uptake of gold. It was therefore concluded that, *Brassica juncea* could be used for phytoextraction of gold and mercury when ammonium thiosulphate is applied to the substrate. Results from the root-crop experiment indicate that, carrots could supersede most of the plants used due to the greater apparent metal-uptake potential.

Finally, a model is proposed for field trials to examine the potential of phytoextraction for gold and mercury in Tanzania. The aim of this model is to examine how the positive results obtained from research conducted in the laboratory and greenhouse can be put into practice. The use of similar plants as well as traditional tropical species (e.g. wild cassava – a known accumulator of cyanide) is suggested along with suitable chemical amendments.

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CHAPTER 1 - GENERAL INTRODUCTION

1.1 Introduction to gold and mercury

1.1.1 Gold in plants

Scientists and alchemists have been researching for centuries without success a 'secret' way of transforming other elements into gold. Gold is mainly used as jewellery, perceived by millions of people in cultures across the world as a "store of value" or a failsafe currency against bad times. For many, it is a personal statement of wealth which has a mysterious market. In times of civil unrest, wars and coups, its value increases. When currencies are weak, the market price of gold tends to increase. When international tension increases, demand tends to rise. When interest rates rise, and inflation seems under control, then the gold market tends to bottom out (Moody 1996). This implies that gold, of all the precious metals, is the most sought after and treasured.

At a different level, scientists have for more than a century been carrying out extensive studies on how gold is taken up by plants. In the 1820s Malte-Brun detected up to 0.6 mg/kg gold in wood ash (Malte-Brun, 1824). Lungwitz, (1900) also reported the presence of gold in plants especially the so called "iron wood" from the Omai Valley in British Guyana. Babicka, (1943) found that seeds of *Clematis vitalba* ('virgins' bower) in the andesitic region of Oslany, Czechoslovakia could accumulate up to 600 mg/kg (ppm) gold in the ash of the seeds. Boyle reports that Babicka, (1943) together with his team also found 610 mg/kg gold in *Equisetum* "marsh horsetail." However, later studies by Cannon *et al.* (1968) showed that horsetails contain on average only 0.17 mg/kg dry weight of gold. This value is about the same as those reported by other scientists and challenged Babicka's analytical methods as having erroneously measured other metals, specifically arsenic, which have high concentrations in *Equisetum* and

taken them as gold values. In 1966 Razin and Rozhkov found up to 19.2 mg/kg gold in different species of bryophytes (Boyle 1979).

Other findings from different scientists Boyle, (1979), Brooks *et al.* (1972, 1977a. 1977b, 1983, 1987, 1998, 1999,) Anderson *et al.* (1998) and Msuya *et al.* (2000) can also be cited. Despite the extensive research work carried out to find natural accumulation of gold in plants, the natural gold content of plants has never been found to exceed 10 μg/kg (ppb) dry weight. Using this criterion, Anderson *et al,* (1998) proposed that the hyperaccumulation of gold in plants to be represented by 1000 (μg/kg) (ppb) in dry mass.

1.1.2 Mercury

The element mercury has been known to exist for many centuries. The first evidence of its use originates from the ancient Chinese, who used the metal and its principal ore cinnabar as a medicine to prolong life, and cinnabar for the preparation of red ink. In the 5th century B.C cinnabar was used as a pigment by the Greek (Kaiser and Tolg, 1980). Aristotle is believed to be the first European to mention it (350 B.C) (Winteringham 1972).

Mercury has unique and curious properties. At warm temperatures, the metal forms a mirror-like liquid of high density, high vapour pressure and consequently of high volatility. Mercury amalgamates well with other metals such as copper, gold, zinc, lead and sometime with definite compounds (e.g. $NaHg_2$) Winteringham, (1972). Like many other compounds, the compounds of mercury appear in rocks, soil, air, water and living organisms by way of a complex system of physical, chemical, and biological controls (Pecora, 1970).

Mercury in soils

Mercury generally occurs in sedimentary and igneous rocks in small quantities. Cinnabar, the sulphide, is the most important mercury-bearing mineral which contains 86% mercury by weight. It is usually formed at low temperatures (< 300^{0}C), and it is

generally found in mineral veins or fractures, as impregnations, or having replaced quartz in rocks near recent volcanic or hot spring areas (Pecora 1970).

According to McLaughlin *et al.*, (1996), there are more than 20 principal mercury minerals existing in nature. Average crustal concentrations of mercury are about 0.08 mg/kg. Generally, this element is more abundant in sedimentary rocks than in igneous rocks (see Table 1.1).

Table 1.1 Mercury concentrations (μg/kg) in major rock types

Rock	Mercury concentration
Igneous rocks	
Basal	0.2-14
Granite	4-28.1
Sedimentary rocks	
Argillaceous sediments	200-400
Shales	180-400
Sandstone	40-100
Limestones, dolomites	40-50

Source: M.J.McLaughlin *et al.* (1996).

Boyle (1979) however, reported that deposits in volcanics tend to contain more mercury than those of sedimentary deposits and younger (Tertiary) deposits tend to be richer in mercury than the older deposits. This is exemplified by the Yellowknife deposits in greenstones and those of the sedimentary area in N.W.T Canada.

Mercury in plants

The study of mercury in plants has of late received more attention than in the past because of the hazards involved in contaminating the food chain. The rate of uptake increases linearly with the content of mercury in the soil. The rate of increase of the mercury content in plants when the soil is the only source of this metal is higher in roots than in shoots (Kabata-Pendias and Pendias, 1992 see Figure 1.1). Studies

conducted by numerous researchers show that mercury is easily absorbed by plants especially the root system. Plants such as lichens, carrots, lettuce and mushrooms have been reported to take up mercury (Kabata-Pendias and Pendias, 1992 see Tables 1.2 and 1.3). Table 1.2 shows that the background level of mercury in vegetables and fruits varies from 2.6 to 86 ppb (DW) and from 0.6 to 70 ppb (FW) respectively (Kabata-Pendias and Pendias 1992).

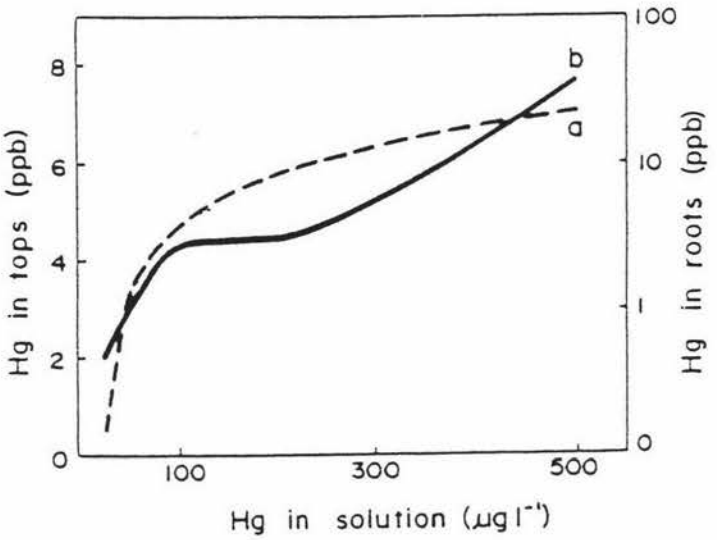


Figure 1.1 Uptake of mercury by 7 day-old oat seedlings from the culture solution of $HgNO_3$ concentration. (a) tops; (b) roots. From: Kabata-Pendias and Pendias (1972).

Toxicology of mercury

Mercury is very poisonous, and is readily absorbed through the respiratory tract, the gastrointestinal tract, or through unbroken skin. Dangerous levels of mercury are readily attained in air, water, plants, fish and soil causing neurological and genetic disorders depending on the route of entry into the body (skin, inhalation, ingestion), and the extent to which it is absorbed. Inorganic protein-bound mercurials are absorbed to a low degree and does detoxify quickly if exposure ceases. However, methyl mercury derivatives are almost totally absorbed causing irreversible lesions (Kaiser and Tolg, 1980).

Table 1.2 Mean mercury content of plant foodstuffs (μg/g) ppb.

Plant	Tissue sample	FW basis	DW basis
Sweet corn	Grains	-	4.6,3
Bean	Pods	70, 17	3, 11
Beet	Roots	3	-
Carrot	Roots	-	86, 5.7
Lettuce	Leaves	<0.6	8.3
Cabbage	Leaves	10	6.5
Potato	Tubers	3, 12	47, <10
Onion	Bulbs	7	<10
Cucumber	Unpeeled fruits	1, 11	-
Tomato	Fruits	1	34, 3.1
Apple	Fruits	10	<10
Orange	Fruits	-	2.6
Lemon	Fruits	43	-
Mushroom	Caps and stalks	-	3.5

Source: (Kabata-Pendias and Pendias 1992)

FW: Fresh Weight

DW: Dry Weight

Symptoms of toxicity

Inorganic mercury:

Inhaled mercury vapour causes injuries to the respiratory tract and the oral cavity e.g. sore mouth, ulcerated gums etc. giving rise to coughing, bronchial inflammation, vomiting, chest pain, excitement, tremors, irritability, diarrhoea and respiratory arrest and death if exposure continues(Kaiser and Tolg, 1980)

Organo-mercury compounds:

These are absorbed to the skin by inhalation and by ingestion. Symptoms include motor disturbances, mental symptoms, congenital malformations and cerebral palsy (Kaiser and Tolg, 1980).

Table 1.3 Mercury concentrations (mg/kg) in plants grown in contaminated sites

Site and pollution source	Plant and part	Maximum or range in content	Country
Metal processing	Edible mushrooms	37.6	Yugoslavia
industry	Carrot, roots	0.5-0.8[a]	Yugoslavia
	Apple, flesh	0.04-0.13[a]	Yugoslavia
	Apple, pips	0.33-1.32[a]	Yugoslavia
Soil overlying Hg	Labrador tea, stems	1-3.5	U.S
deposit	Carrot, roots	0.05-0.1[a]	Yugoslavia
Chlor-alkali or	Lettuce, leaves	0.15-0.36	Switzerland
chemical works	Spinach	0.11-0.59	Switzerland
	Corn, grains	0.074-0.136	Switzerland
	Wheat, grains	0.007-0.025	Switzerland
	Festuca rubra	4.0	Great Britain
	Lichens	36.0	Finland
	Lettuce leaves	0.1[a]	Canada
Urban vicinity and	Bryophytes	1.4	U.S
parks	Edible mushrooms	33.6	Switzerland
Sludged or irrigated	Brome grass, tops	0.09-2.01[b]	Canada
farmland	Brown rice	4.9	Japan
Application of	Potato, foliage	1.1-6.8	Canada
fungicides or Hg	Lettuce, leaves	0.1-0.3	Canada
salts	Oat, grains	631[c]	Sweden
	Oat, straw	99[c]	Sweden
	Wheat, grains	0.05-0.17[d]	Poland

Source: Kabata-Pendias and Pendias (1992)

[a] Fresh Weight basis.

[b] Different Hg compounds added to soil columns

[c] Pot experiment.

[d] After Hg treatment of seeds.

Maximum Allowable Concentration (MAC-values) of mercury and its compounds

The maximum allowable concentration of mercury is defined as "that average concentration in the air which causes no signs or symptoms of illness or physical impairment in all but hypersensitive workers during their working day (8hr/5days a week) on a continuing basis as judged by the most sensitive internationally accepted tests"(see Table 1.4). Air saturated with mercury vapour at 20^0C contains a concentration that exceeds the toxic limit. The higher the temperature the higher the danger(Kaiser and Tolg, 1980).

Table 1.4 Maximum allowable concentrations of mercury and its inorganic and organic compounds.

Mercury/Hg-compound	MAC(mg/m^3) Western countries	MAC(mg/m^3) Russia
Mercury vapour	0.1	
Inorganic compound	0.1	0.01
Organic compound	0.01	
Alkyl mercury salts		0.005

Source: Kaiser and Tolg (1980)

Plants growing in environments with very small amounts of mercury in the soil seldom have mercury concentrations exceeding 0.5 mg/kg mercury in their tissues. Areas with a very high mercury occurrence in the environment may have mercury in plants to the order of 3.5 mg/kg in dried tissues. Rankama and Sahama (1950) stated that "droplets of metallic mercury have been found in the seed capsules of *Holosteum umbellatum* (jagged chickweed; family Caryophyllaceae) growing on some mercury-rich soils" (Pecora 1970). According to Pecora, Goldschmidt (1954) reported the occurrence of drops of metallic mercury under the moss cover of the forest floor near hydrothermal mercury deposits in the Rhine Palatinate region (Pecora 1970).

The toxicity of waterborne mercury to humans was emphasised over 50 years ago when 50 persons out of more than 100 affected in Japan died of the strange "Minamata Disease." Investigations confirmed that they died from mercury-contaminated fish

obtained from Minamata Bay which had received large amounts of methyl mercury compounds in the waste flowing out from a plastics factory (Pecora 1970).

1.2 Heavy metals

The term heavy metals is widely used here to refer to all metals excluding the alkali metals, alkali earth metals and aluminium. The metalloids arsenic, antimony and selenium are often included (Streit and Stumm, 1993).

In nature, heavy metals exist in soils by way of weathering of the parent rocks. However, human practices are by far the most contributive to heavy-metal contamination in the environment. These are derived from practices associated with mining and smelting of ores or smelting of scrap metals, or industrial and municipal waste disposal. Once in the soils and water, heavy metals such as mercury, lead, copper, zinc and cadmium accumulate in the food chain through plants and animals causing harm to flora and fauna (Iskandar and Adriano, 1997).

Mining activities accelerate weathering of minerals, especially unoxidised sulphide ores which would have otherwise remained stable if they had not been exposed to oxygen and humidity. The constant increase in global demand for minerals such as gold (In 1992 global demand was 3,573 tonnes, in 1995 it was 3,642 tonnes –Moody, 1996), lead to expanding mining operations. Unfortunately, in developing countries where most of the gold comes from artisanal mining (defined as low cost mining method where someone uses simple rudimentary skills to achieve a certain objective without applying expensive conventional methods), hazards and health effects of mercury and other heavy metals are not addressed. In Africa, it is estimated that small-scale miners (better known as artisanal miners) produce up to 20% of the gold (Moody, 1996). Many transnational corporations and junior mining companies are jostling in staking claims in developing countries. It is estimated that 70 countries, including 31 in Africa, have changed their mining laws to attract foreign companies. Countries such as the Philippines and Ghana are holding out a package of incentives such as reduced taxes

and lifting of foreign ownership restrictions (Moody, 1996). If developing countries are to benefit from gold mining, then economic and environmental safeguards are imperative. The use and development of non-polluting technologies, better environmental monitoring and remediation of contaminated sites need to be undertaken.

1.2.1 The chemistry of gold

Of all the metals known today, gold is one of the most noble, being not significantly attacked by either oxygen or sulphur. In nature, metallic gold occurs in two forms. Placer or alluvial gold consists of weathered auriferous rock that has been washed and deposited in riverbeds. Gold's high specific gravity (19.3) compared to its host rock (2.3) results in the lighter rocks being washed away. Once discovered, this type of gold is easier to process because it appears in the form of nuggets or particles. Reef or vein gold occurs as microscopic particles in quartz or albite rocks often associated with iron pyrites (Puddephatt , 1978).

Depending on the ocean depth, the concentration of gold in seawater is thought to be $2x10^{-11}M$. Calculations based on the redox potential of gold compounds and composition of seawater suggests that gold (1) complex ion $[AuCl_2]^-$ predominates and other smaller amounts of $[AuClBr2]^{-2}$ (Puddephatt, 1978).

Gold reacts with all the halogens, bromide being the most reactive. Below 130^0C, chloride is adsorbed on to the surface and forms surface compounds. Above 200^0C, a high reaction rate is achieved giving a sublimation of chloride and leaving a clean gold surface.

Although gold may not appreciably dissolve in nitric or hydrochloric acid it will readily dissolve in *aqua regia* ($HCl:HNO_3$) to give tetrachloroauric acid $H[AuCl_4]$.

1.2.2 The chemistry of mercury

Mercury, the only metal which occurs in liquid form at ordinary earth surface temperatures has a chemical symbol Hg derived from the Latin name hydrargyrum, i.e., liquid silver, or "argentium vivum" meaning live or quick silver. The atomic weight of mercury is 200.59 and its density is 13.595 g/cm^3 at 0^{0}C. Its solubility in water at 25^{0}C is 6x10^{-6} g/100mL. Like other metallic elements, mercury reacts with a great variety of organic and inorganic compounds to form simple and complex molecules ranging from cinnabar, a mercury sulphide and the most common ore mineral, to the metallo-organic complexes which have been classified as potential water pollutants and biological toxins (Pecora, 1970).

At 0^{0}C, mercury has a vapour pressure of 0.189x10^{-3}mm; at 20^{0}C it has vapour pressure of 1.22x10^{-3}mm, and at 30^{0}C it has vapour pressure of 2.8x10^{-3} mm. On account of the high vapour pressure, mercury evaporates quickly into the air after being spilled. It can be removed from an enclosed room by sucking it through a filter consisting of different layers of $CaCl_2$, NaI, and activated carbon. Laboratory air can be decontaminated by gassing the room with H_2S and by covering the floor and the benches with H_2S-water. Iodised carbon has also proved useful. Spilt or splashed mercury can be collected with a capillary connected to a glass container and a pump. Air saturated with mercury vapour at 20^{0}C contains a concentration that exceeds the toxic limit (Kaiser and Tolg 1980). Mercury becomes solid when subjected to a pressure of 7640 atmospheres (about 5.8x10^6 torrs) and this pressure is used as a standard in measuring extremely high pressures. The metal dissolves in nitric or concentrated sulphuric acid but it is resistant to alkalis.

Mercury is very reactive and following release into the soil environment, rapidly forms complexes with soil constituents. Mercury is different to other metals such as cadmium and zinc because of its reactivity and tendency to hydrolyse. Both Hg^{2+} and Hg^{+} ions are present at pH values commonly encountered in soil. Although the Hg^{+} ion is only a small fraction of the total mercury concentration, it increases 10 times with each unit rise in pH (McLaughlin *et al.*, 1996).

Mercury has a tendency to form complexes with Cl^-, OH^-, S^{2-} and S^- in functional groups of organic ligands (McLaughlin *et al.*, 1996). The organo complexes of mercury, especially the methylated forms, are of great importance in the environment and contribute to its general mobility and subsequent uptake by various organisms. Toxicity of mercury is in the order $CH_3HgCH_3>CH_3Hg+>Hg^{2+}>Hg^{+}>Hg^{0}$, the methylated complexes being extremely toxic.

Adsorption of mercury, which is a result of its release into the soil system in inorganic form, depends on many factors. Among them are the chemical form of mercury applied, the nature of the soil constituents, soil pH, types of cations on the exchange complex, redox potential, composition of the background electrolyte and the textural class of the soil. The sorption (absorption and adsorption considered jointly) maximum for mercury ion occurs at the pH range 4.0-5.0 (McLaughlin *et al.*, 1996).

1.2.3 The Tui base-metal mine tailings

The Tui mine tailings represents one of the few badly contaminated environments in New Zealand with a substrate concentration of heavy metals high enough to warrant phytoextraction studies. Located on the flanks of Mount Te Aroha in the Coromandel district of the northern part of the North Island, New Zealand, the mine has had a long history of exploration and productive mining (Figure 1.2). The most recent period of activity was in 1974 when 100 tonnes of ore was being processed daily, yielding up to 10 tonnes of a Pb-Cu-Zn concentrate containing minor amounts of Cd-Ag-Au (Cochrane, 1969). The closure of the mine in 1974 left a tailings dam with 100,000 m^2 of tailings with high levels of heavy metals (Morrell *et al.*, 1996). The tailings continue to oxidise, producing acid mine drainage (AMD). The principle metal-bearing minerals present in the Tui ore are: galena (PbS), sphalerite (ZnS) and chalcopyrite ($CuFeS_2$). Less abundant are the cadmium, sulphides, greenockite and hawleyite. Lead in the Tui mine tailings has been oxidised *in situ* to an anglesite ($PbSO_4$) mineral phase. Although in many reports mercury has not been cited, it is present at small concentrations of about 2 mg/kg.

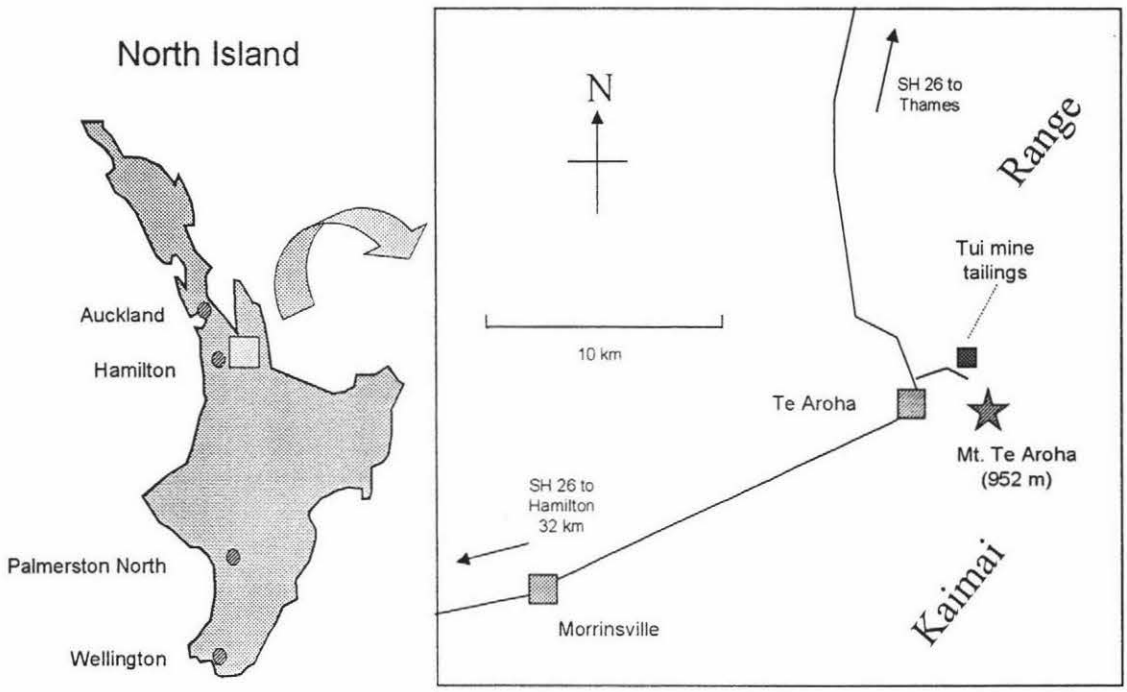


Figure 1.2. Map of the North Island of New Zealand showing the location of Tui mine tailings.

1.3 Contamination and pollution

Contamination of soils with a group of toxic metals generally referred to as "heavy metals," is a national and an international problem. Contamination may have different forms depending on the concentrations of metals in the soil. Contamination here is taken to mean the presence of metals in soils at concentrations above average background. Such contamination may be either *natural* or *anthropogenic* (due to human activities such as mining, agriculture waste disposal etc) in origin although there is no fixed "threshold criterion" for contamination that can be quantified. The negative impact of metal on the health of flora and fauna can be taken to represent pollution. Polluted land is contaminated land; however, contamination does not necessarily constitute pollution (Anderson 2000).

In some countries, regulatory agencies require that the metal concentration be reduced to specified lower levels. Typical background concentrations for a number of metals are given in Table 1.5

Table 1.5. Native soil and regulatory sewage sludge application concentrations of metals in soils and Toxic Characteristic Leaching Procedure regulatory limits for hazardous waste characterisation.

Metal	Normal[+] range for Soil (mg/kg)	Maximum[++] cumulative load from Regulation No 503 (mg/kg)	TCLP regulatory limit (mg/L)
Arsenic	1-50	41	5.0
Beryllium	0.1-40	-[+++]	1.0
Cadmium	0.01-0.7	20	5.0
Chromium	1.0-1,000	1,540	-
Copper	2.0-100	770	5.0
Lead	2.0-200	300	0.2
Mercury	0.01-0.3	17	-
Molybdenum	0.2-5.0	9	-
Nickel	5.0-500	220	1.0
Selenium	0.1-2.0	51	-
Zinc	10-300	1440	

Source: Iskandar and Adriano (1997)

[+] From USEPA. 1983. Hazardous Waste Land Treatment SW 874, pp. 273.

[++] Calculated from 40 CFR Part 503 regulations assuming a soil bulk density of 1.30g/cm^3 and a 15 cm depth of soil

[+++] Not applicable. Source: Iskandar and Adriano (1997)

TCLP Toxic Characteristic Leaching Procedure

1.4 Remediation

Remediation of contaminated soils is stimulated by regulatory pressure and public concern. Several methods are available to decontaminate soils containing high concentrations of heavy metals. These are physical and/or, chemical techniques and, of late, plant-based techniques such as *phytoremediation*. Russel *et al.* (1991) compared the phytoremediation method to the other conventional methods and found that phytoremediation costs less than US$100,000 per hectare to remove metals in comparison with $US 100,000 to 1,000,000 per hectare using conventional methods.

According to Russel the expected cost for the clean-up of heavy metal polluted sites over the next 30 years in the USA alone is $US 750 billion.

1.4.1 Conventional technology

Conventional treatment methods for contaminated soil include removal, covering contaminants with clean soil and inerting. Inerting is the process whereby heavy metals are chemically altered to a state where their effect on the environment is minimised (Robinson,. 1997). Removal of contaminated soils may involve a large transportation and excavation cost as the contaminated soil will still need to be stored somewhere. Covering with topsoil may allow vegetation growth but will not prevent soil erosion and metal leaching. Covering with concrete makes the site unsuitable for agricultural use. When acids are used to leach metals in dumps, the operation becomes much cheaper because transportation costs are reduced or even avoided. However, this procedure may lead to contamination of the local waterways, which may cause other secondary environmental problems. Inerting can also be achieved through the use of soil amendments which chemically alter some metals by reducing them to a less toxic state. Unfortunately, this only applies to very few metals such as chromium and lead (Ma *et al.*, 1995).

1.4.2 Emerging technology

Decontamination of soils contaminated with toxic metals using plants is a fairly modern technology, that still requires extensive field trials. It promises to be environmentally friendly and may eventually be cheap alternative to conventional methods. Chaney (1983) suggested that hyperaccumulator plants may be used to remove heavy metals from polluted soils, technology that has been named *phytoremediation*. The best approach would be to use plants which are metal-tolerant and at the same time have a high biomass. In such cases the best suited are native plants because they have already proved that they can withstand the existing environmental conditions regardless of how toxic the soils are.

Another emerging technology is the rhizofiltration. This concept which was introduced by Dushenkov *et al.* (1995) is a process in which the roots of terrestrial plants are used to extract toxic metals or radionuclides from polluted aquatic systems. Rhizofiltration is seen as an improvement over *aquatic phytoremediation* (using aquatic plants to extract metals from polluted water) because of the superior biomass production of the terrestrial plants (Robinson, 1997).

Phytovolatilisation which is a process where some toxic elements can be converted to gaseous compounds and removed from polluted soils via plants as termed by Zayed *et al.* (1995), is another emerging technology. Zayed investigated the phytovolatilisation of selenium which is a common pollutant of industrial sites.

1.4.3 Other applications of plant-based technology

Perhaps the most significant tool in phytoprospecting will be the use of plants in mineral exploration, a process called *geobotanical prospecting.* The presence of *Becium homblei* from Central Africa was used to delineate copper deposits in the Zambian Copper Belt (Howard Williams, 1970). *Astragalus* species was used by scientists at the U.S Geochemical Survey to find areas of uranium mineralisation (Cannon, 1960). The genus *Astragalus* contains several species that hyperaccumulate selenium which is geochemically associated with uranium.

Brooks and Johannes, (1990), described *Phytoarchaeology* as the process whereby the presence of plants is used to investigate some archaeological event. Copper that was smelted in Central Africa by ancient artisans has left some localised copper pollution around the working sites. Hyperaccumuulators of copper such as *Haumaniastum katangense* and *H. robertii,* are used by archaeologists to search for ancient copper artefacts (Plaen *et al.* 1982). According to Brooks (1997), there is a colony of *Alyssum corsicum* growing over the ultramafics at Bastia. It is believed that the seeds were brought along with cargoes of wheat, showing the existence of ancient Venetian trade routes.

1.5 Hyperaccumulation

By nature, almost all plants remove metals from their surroundings. Some of the metals may be essential to the plant for its life cycle, and others may be harmful to the plants. Brooks (1983) divided the elements into essential and non-essential, depending on whether the plants can survive without them. Plants responses to essential elements can be divided into three categories according to increasing elemental concentrations: (1) deficiency, (2) optimal, and (3) toxicity. Non-essential elements are tolerated by plants at low concentrations and may be toxic at higher concentrations (Robinson, 1997).

1.5.1 Natural hyperaccumulation

Natural hyperaccumulation is the ability of some plant species to accumulate inordinately high levels of one or more heavy metals. This was first reported by Baumann (1885) for zinc accumulation by *Thlaspi calaminare* growing near Aachen, Germany. The first quantitative record for any other metal was made in Italy by Minguzzi and Vergnano (1948), with regard to nickel accumulation by the small perennial shrub *Alyssum bertolonii*. These workers reported a nickel content of 0.79% (7,900 mg/kg) in the dry leaves of plants growing in soil containing only 0.42% of this metal.

Brooks *et al.* (1977a) used the term *hyperaccumulation* to describe this unusual plant character. At that time, the threshold concentration was set at 1,000 mg/kg (0.1%) dry weight for most metals, with the exception of zinc, for which the threshold was set at 10,000 mg/kg (1%). The more modern accepted threshold criterion is accumulation 100 times greater than in non-accumulator plants growing in the same environment. At present there are about 400 species of known terrestrial plants that hyperaccumulate one or more heavy metals. There are 315 species which hyperaccumulate nickel, 26 cobalt, 24 copper, 19 selenium, 18 zinc, 8 manganese, 2 cadmium and 2 thallium (Brooks, 1998). There are no natural hyperaccumulators of gold or mercury known so far (Table 1.6).

Table 1.6. Specific hyperaccumulators that might be used for phytomining

Element	Species (few examples)	Concentration (mg/kg dry weight)	Biomass (t/ha per year)
Cadmium	*Thlaspi caerulescens*	3000(1)	4
Cobalt	*Haumaniastrum robertii*	10,200(2)	4
Copper	*Haumaniastrum katangense*	8,356(1)	5
Lead	*Thlaspi rotundifolium* subsp	8,200 (5)	4
Manganese	*Macadamia neurophylla.*	55,000 (400)	30
Nickel	*Alyssum bertolonii*	13,400 (2)	9
	Berkheya coddii	17,000 (2)	18
Selenium	*Astragalus pattersoni*		
	Iberis intermedia	6,000 (1)	5
Thallium	*Atriplex confertifolia*	3,070 (1)	8
Uranium	*Thlaspi calaminare*	100 (0.5)	10
Zinc		10,000 (100)	4

Source: Brooks *et al.* (1998)
Concentrations are mean highest elemental values (mg/kg dry matter). Natural levels shown in parentheses.

1.5.2 Induced hyperaccumulation

Uptake of metals that are not 'naturally' accumulated by any recognised plant species can still be effected using phytoextraction technology. If a chemical amendment added to soil 'targets' certain insoluble metals, these metals can be 'induced' into the soil solution. Plants often accumulate this soluble metal complex passively through transpiration (induced hyperaccumulation), although the exact mechanisms for induced-metal uptake are poorly understood and are a matter of some debate.

Normally, plants grown under hydroponic (in solutions) conditions will passively takeup metal ions. Shacklette *et al,* (1970) reported uptake of gold in cuttings of *Impatiens* spp. and *I. holstii* grown in solutions of gold chloride, cyanide, bromide, iodide, thiocyanate and thiosulphate for 24 to 48 hrs (Table 1.7).

Table 1.7. Gold concentrations (mg/kg dry mass) in cuttings of *Impatiens balsamina* and *I. holstii* immersed for 48 hours in solutions of gold salts at different pH values.

Gold salt	pH	*I. balsamina*	*I. holstii*
Cyanide	11.0	32	320
	7.7	32	4.2
	6.5	260	130
Chloride	6.2	7.5	7.0
Bromide	6.2	160	55
Iodide	6.0	45	33
Thiocyanate	6.2	<0.4	<0.8
Thiosulphate	6.2	28	6.6

Source: Shacklette *et al.*, (1970)

Following this successful experiment by Shacklette *et al.* (1970) on the use of thiocyanate, other scientists developed interest and pursued further research on induced uptake of gold by plants on non-hydroponic substrates. Work by Anderson *et al.* (1998), later reviewed in 1999, induced uptake of up to 57 mg/kg gold in dried leaves of *Brassica juncea* (Indian mustard). They proposed the possibility of using *B. juncea* or other plants to carry out phytomining for gold by growing crops over mine tailings or other suitable substrates. *Brassica juncea* is believed to produce high rates of biomass under field conditions and also has the capacity to accumulate substantial metal concentrations in the shoots. Anderson's successful research work led me to be interested in this research project.

In the course of later experiments, I observed that gold concentrations in plants tended to be higher in the roots than the above-ground shoots when thiosulphate or thiocyanate-induced gold uptake was initiated. I therefore carried out experiments on accumulation of gold using harvestable root crops including radish, beet root, onion and carrot.

1.6 Phytoextraction (phytomining and phytoremediation)

The realisation of hyperaccumulation of metals by some plants has led scientists to further research work on phytoextraction. Phytoextraction is a very broad topic, which in here it can simply be used to describe two types of operations, phytomining and phytoremediation. Phytomining unlike phytoremediation is a more recent advance on phytoremediation technology where a target metal is of sufficient economic value to warrant recovery of that particular metal from plant material (Baker and Brooks, 1989; Anderson, 2000). A phytoextraction operation is summarised in Figure 1.3.

The concept of phytoextraction, which is shown in a simplified diagram in Figure 1.3, involves 3 steps:

1. growing of plants that can accumulate metals (natural or induced hyperaccumulation) from an area of metalliferous land,
2. harvesting and burning of the metal-rich biomass, and
3. smelting (phytomining) or disposal (phytoremediation) of the ash

It is of double benefit if a single plant can be used for both phytomining of a particular metal (e.g gold) and at the same time be used for phytoremediation (e.g mercury).

1.6.1 Phytoremediation

Phytoremediation is a term used to define the use of hyperaccumulator plants *in situ* to remove heavy metals in contaminated soils without consideration of commercial gain (Baker and Brooks, 1989). After the plants have accumulated enough metal, they are harvested and burnt, thus reducing the polluting metal to a small volume called a *bio-ore* that can safely be disposed of as landfill at a monitored site/pit.

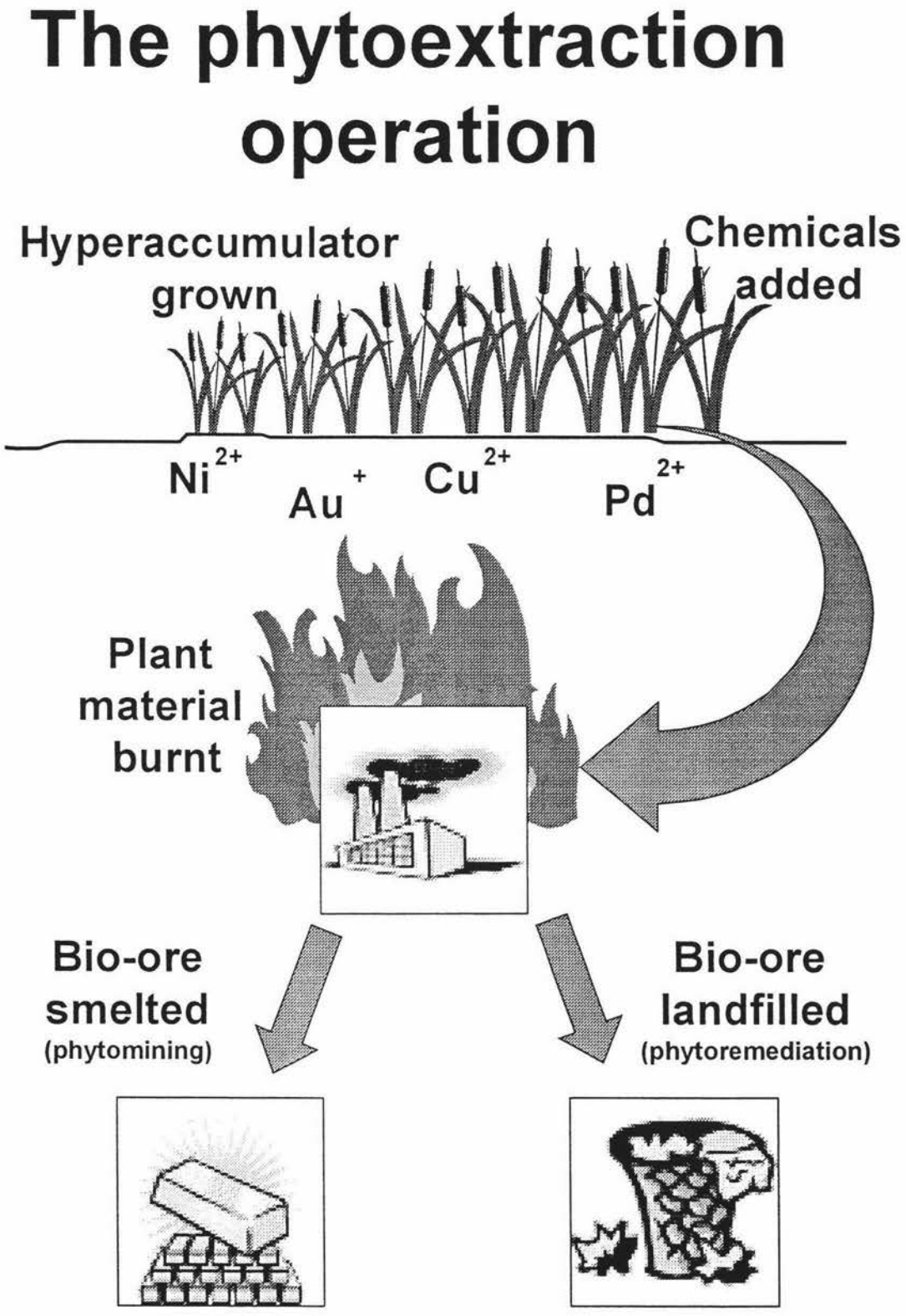


Figure 1.3. Diagrammatic representation of the phytoextraction operation.

1.4.2. Phytomining

The idea of using plants to remove metals was first proposed by Chaney (1983) and later by Baker and Brooks (1989) who used the term *phytomining*. However, field trials for nickel were not undertaken until later, when Nicks and Chambers (1995) working from Nevada grew a "crop of nickel" in California over nickel-rich 'serpentine' soil. These ultramafic (ultra-magnesium-ferric) soils are derived from ultramafic rocks that cover about 1% of the Earth's crust and contain high concentrations of nickel, chromium, cobalt and magnesium. A phytomining operation is summarised in Figure 1.4.

The aim of the research described in this thesis was to investigate the environmental implications of phytoextraction for mercury and gold and toxic heavy metals that contaminate the environment. This was done with a practical idea of remediating mercury in areas where artisanal gold mining is rampant and with a view of phytomining gold by using the same plants.

Laboratory and greenhouse research work was conducted using Tui mine tailings as a substrate and at times using an artificial gold substrate consisting of 3.8 mg/kg of elemental gold impregnated in well-sieved sand. Artificial gold was chosen so as to overcome the problem of non-homogeneous distribution of gold, metal toxicity and pH conditions that often inhibit plant growth in acidic mine-waste material. Different root plants such as carrots, red beet, onion and oriental radish were chosen for this experiment. Tui mine tailings were selected for this experiment because of their longstanding history of contamination and research work done on the area (Morrell, 1997).

Other plants used in the experiments were *Brassica juncea, Berkheya coddii,* lucerne, chicory, *Alyssum bertolonii* and *Linum* sp.

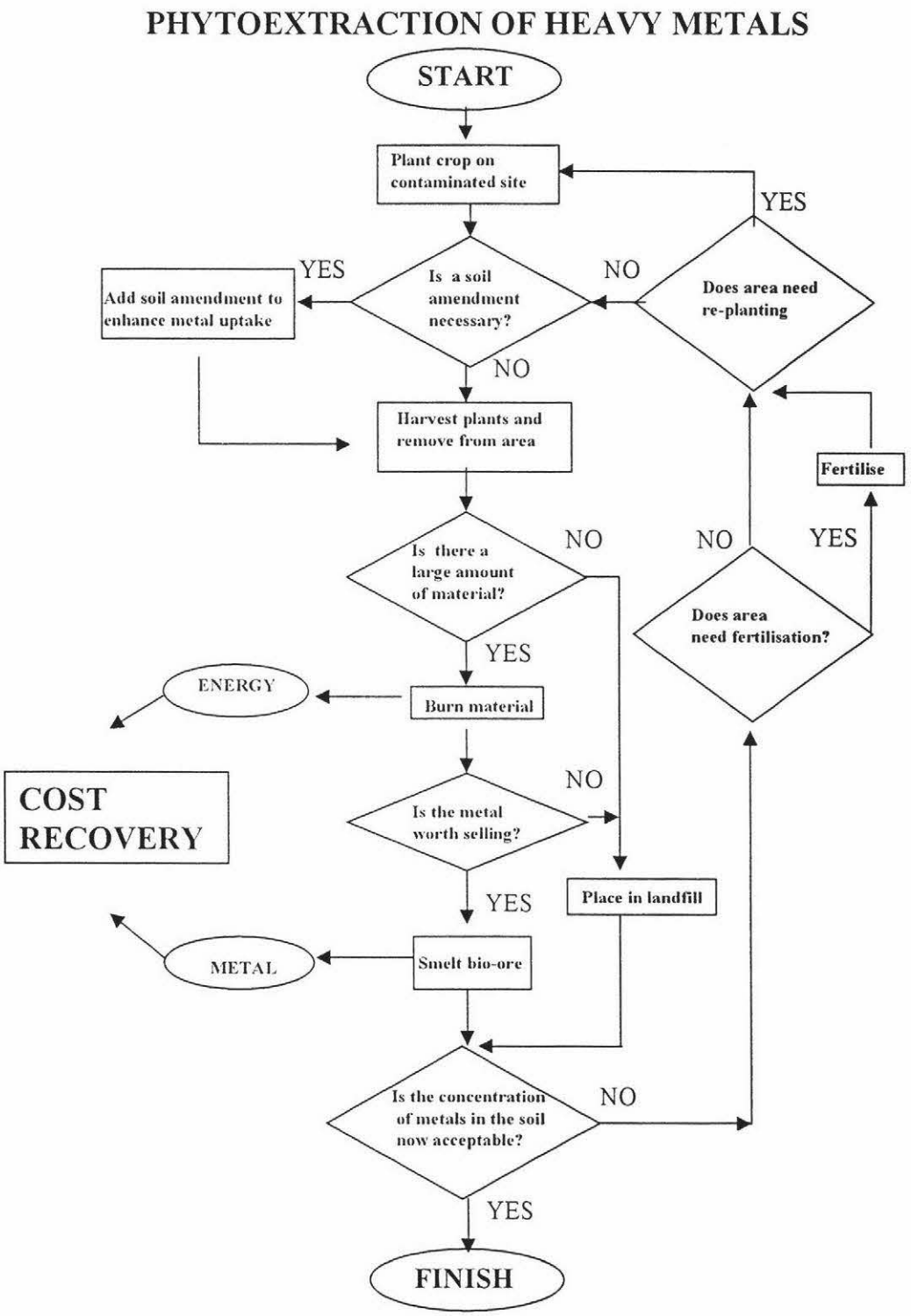


Figure 1.4. Flow diagram showing phytoextraction operation (after Robinson 1997).

CHAPTER 2 - ANALYTICAL METHODOLOGY FOR GOLD AND MERCURY DETERMINATIONS USING FLAME ATOMIC ABSORPTION SPECTROMETRY (FAAS), GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY (GFAAS) AND FLAMELESS ATOMIC ABSORPTION SPECTROMETRY

2.1 Introduction

Gold can be quantified by use of flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS). According to Brooks, (1983), Walsh (1955) was one of the early pioneers to develop the technique of FAAS and it has since become a popular method of elemental analysis. The type of instrument to be used will depend on the type of sample and concentration of gold in the analyte. After digestion with acids, high levels of gold (>1 mg/L) can easily be detected by FAAS. Low levels of gold (< 1 mg/L) may require extraction of the gold into methylisobutyl ketone (MIBK) and determination by GFAAS. Mercury, on the other hand is quantified using flameless atomic absorption spectrometry due to its high volatility (Boiling point 357.3^{0}C and Melting point -38.9^{0}C).

2.1.1 Use of organic solvents

Solvent extraction involves the distribution of a solute between two immiscible liquid phases. Solvent extraction technique is very useful for rapid and clean separation of both organic and inorganic solutes. For metals, many methods of quantification involve some separation procedure in order to remove the analyte from interfering signal and to increase its concentration to an appropriate level (Brooks 1992). Methylisobutyl ketone (MIBK) is one of the best solvents for extraction and aspiration used in the GFAAS.

When organic solvents are aspirated into a flame, an oxidising (fuel-lean) flame must be used, because the solvent must be burned. The extraction of an analyte into an organic phase from an aqueous solution is represented by the expression:

$$K_d = [X]_o/[X]_a$$

where: K_d = the distribution coefficient

$[X]_a$= the concentration of the analyte in the aqueous phase

$[X]_o$= the concentration of the analyte in the organic phase

Expressed as a percentage, the extraction is given by the expression:

$$E = 100K_d/[K_d + (V_a/V_o)]$$

Where : E = the % extraction, V_a and V_o are the volume of the aqueous and organic phases respectively.

Values of K_d >1000 are quite common for some extraction systems, and in the case of the extraction of gold chlorocomplexes into MIBK, K_d is of the order of 10^6; i.e.99% of the gold would be extractable with an aqueous/organic phase ratio of 10,000.

2.2 Analytical techniques for gold and mercury determinations

2.2.1 Flame atomic absorption spectrometry (FAAS)

Flame atomic absorption spectrometry works on the principle that the sample solution is aspirated into a flame and the analyte is converted to atomic vapour. The flame then contains the atoms of that element. Some are thermally excited by the flame, but most remain in the ground state which in turn can absorb radiation given off by a special source made from that element. The wavelength of radiation given off by the source is the same as that absorbed by the atoms in the flame. A simplified schematic diagram of AAS is shown in Figure 2.1.

Absorption in atomic absorption spectrometry follows Beer's law. That is absorbance is directly proportional to the concentration of atomic vapour in the flame.

$$A = ecl$$

Where: A = absorbance, e = absorption coefficient l = path length

and c = concentration of the analyte in the solution

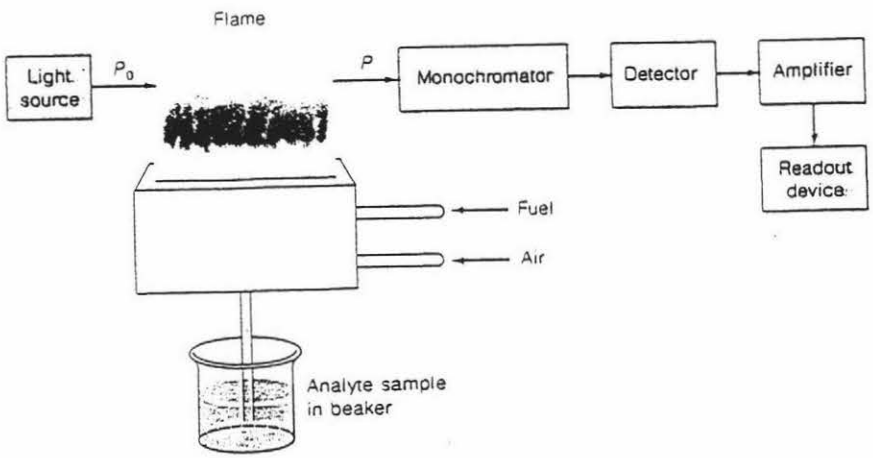


Figure 2.1. Schematic outline of an atomic absorption spectrometer.

Some important components of an atomic absorption spectrometer illustrated in Fig. 2.1 are:

Source. The source used in FAAS is a hollow-cathode lamp. This is a sharp line source that emits the lines of the element to be analysed. These possess the precise energies required for absorption by the analyte. The basic construction is illustrated in Figure 2.2.

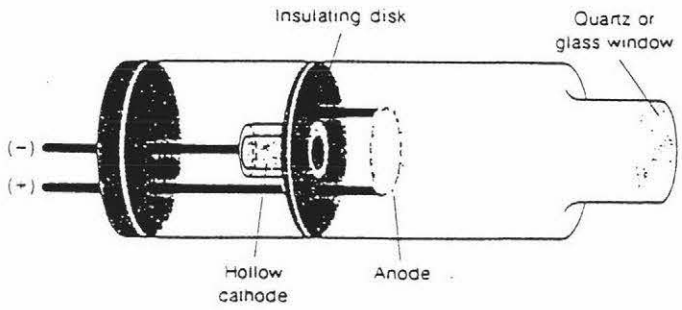


Figure 2.2. A hollow-cathode lamp

Burners. The two basic burners in use in the FAAS are (i) the total consumption burner and (ii) the premix chamber burner. which is most commonly used. The total consumption burner uses the entire aspirated sample but it has a shorter path length and many large droplets are not vaporised in the flame. It is mainly used to aspirate viscous and "high solid" samples such as urine and undiluted serum. Most flame atomic absorption spectrometers use a premix burner which is limited to a low-burning velocity flame but the "atomisation efficiency" (efficiency of producing atomic vapour) is greater. Compared with the total consumption burner, the premix burner is less noisy. The sample solution is drawn into the nebuliser by the rapid flow of oxidant (usually air) past the tip of the sample capillary. The liquid breaks into a fine mist as it leaves the tip of the nebuliser. The spray is directed at high speed against a glass bead, upon which the droplets are broken into even smaller particles which are subsequently atomised in the flame.

Flames. The air-acetylene flame is the most popular for FAAS. The nitrous oxide-acetylene flame is best for refractory elements (high vaporisation temperature). When a hotter flame is required, the acetylene-nitrous oxide combination is usually used. The main flames that are used for atomic absorption are listed in Table 2.1. Hotter flames are needed for refractory elements or to decompose such species as metal oxides formed during passage through the flame.

Table 2. 1. Maximum flame temperatures

Fuel	Oxidant	Temperature (K)
Acetylene	Air	2400-2700
Acetylene	Nitrous oxide	2900-3100
Acetylene	Oxygen	3300-3400
Hydrogen	Air	2300-2400
Hydrogen	Oxygen	2800-3000
Cyanogen	Oxygen	4800

Source: Harris (1986)

Interferences

In AAS measurements, interference (the effect that changes the signal when analyte concentration remains unchanged) is widespread. Interferences fall under the following categories

Spectral: These are unwanted signals overlapping analyte signal. The signals can be due to other elements or molecules in the sample or with signals due to the flame or furnace. The best means of dealing with overlap between lines of different elements in the sample is to choose another wavelength for analysis.

Ionisation: Ionisation of analyte atoms decreases the concentration of neutral analyte atoms in the flame. This can be corrected by adding an ionisation suppressor. This is an element added to a sample to decrease the extent of ionisation of the analyte.

Refractory compound formation: Chemical reactions decrease the concentration of analyte atoms. This can be avoided by chemical competition or by use of a high-temperature flame. A more useful flame for these elements is the nitrous oxide-acetylene flame.

Physical: These are different parameters which affect the rate of sample uptake in the burner e.g variation in the gas flow rate, variation in sample viscosity due to temperature or solvent variations, high solids content and changes in the flame temperature. These can be reduced by reducing the sample volume, lengthening the drying program and flash volatilising the sample (hot injection).

The gold cathode lamp is set at 5.0 mA with a 242.8 nm wavelength and slit width of 0.5 nm.

2.2.2 Graphite furnace atomic absorption spectrometry (GFAAS)

The principles of GFAAS are similar to those of FAAS. However, the flame cell of the GFAAS is replaced by a small graphite tube, positioned in the path of the radiation from the hollow cathode lamp. Each end of the oven is a window through which the light beam travels. The analyte is introduced in the graphite tube through a small hole along the upper side of the suspended tube by a probe. A simplified schematic of a typical GFAAS is in Figure 2.3.

The electrically heated furnace offers greater sensitivity than that afforded by FAAS because the entire sample is confined in a light path for a few seconds compared with the residence time of microseconds that a given atom is present in the flame of FAAS. GFAAS requires a smaller volume (as little as1 μL of sample) whereas FAAS requires larger volumes (1-2 mL) because the sample is constantly flowing into the flame. However, GFAAS demands more operator skill and greater effort to determine the proper conditions for each type of sample because the furnace must be heated in three or more steps to properly atomise the sample.

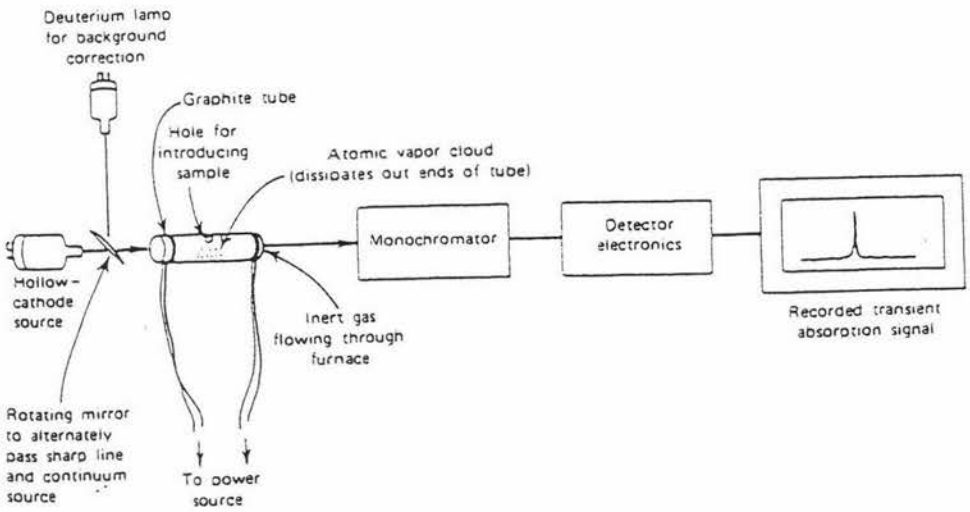


Figure 2.3. Schematic outline of a GFAAS

The first step in the furnace after setting, starts with heating. A small voltage is applied to the two electrodes and the tube is heated to a temperature of perhaps 70°C. The temperature is then raised to about 120°C in the second step in accordance with the preset graphite furnace parameters. In the next stage, the tube is heated to a higher "charring" temperature, typically to 400°C, in order to remove volatiles and any organic material. When MIBK is used (specifically for gold), the charring temperature is maintained at 300°C. Finally, the analyte is atomised by raising the temperature to 2500°C (sometimes even as high as 3000°C). Samples to be analysed are placed in small cups placed on a turntable (the maximum number of cups depends on the type of machine). The injecting speed, the number of replicates and the number of loadings are programmed to run automatically. In GFAAS, the signal is controlled not only by the atomisation temperature, but also by the rate at which the temperature is achieved (ramp time). A typical sequence of steps (graphite furnace parameters) for a GFAAS program is given in Table 2.2.

Table 2.2. Program used for determination of gold using GFAAS for graphite furnace and MIBK.

Main Control
System Type Furnace
Load A Application Parameters
Graphite Furnace Parameters

Step	Final Temp. (C)	Ramp Time (s)	Hold Time (s)	Gas Type	Read	Signal Graphics
Step 1	70	5.0	2.0	Inert	Off	Off
Step 2	120	6.0	10.0	Inert	Off	Off
Step 3	180	5.0	3.0	Inert	Off	Off
Step 4	300	5.0	15.0	Inert	Off	Off
Step 5	2500	1.1	2.0	None	On	On

Interferences in the GFAAS

Background correction:

Some samples produce particulate matter (smoke or unvaporised particles), which scatters a significant fraction of light from the hollow-cathode lamp. Smoke is particularly bad for graphite furnaces. The detector cannot distinguish scattering from absorption, so this can lead to a systematic error in the measurement of analyte. A deuterium lamp (D_2) having a broad-band output is used for background correction. Analysis of gold standards are shown in Table 2.3.

Table 2.3. Calibration table for fig. 2.4

Furnace
Application Parameters
Name MSUYA AU
Calibration Table

	Standard Concentration	Mean Standard Reading
Standard 1	100.000	0.503
Standard 2	200.000	0.872
Standard 3	400.000	1.358

As with FAAS, the gold cathode lamp is set at 5.0 mA with a 242.8 nm wavelength and slit width of 0.5 nm. The calibration curve is shown in Figure 2.4 and the calibration programme in Table 2.3. The peaks for different concentrations of gold are shown in Figure 2.5. Apart from a few occasional problems with the deuterium background correction in the AAS, and deterioration of absorbance signal, the equipment performance was excellent.

Parameters specific for the analysis of gold

Calibration curve for gold

The most common technique for quantitative analysis (in both FAAS and GFAAS) is to construct a standard working curve, such as that shown in Figure 2.4. The idea of constructing a working curve is to calibrate the machine. In real practice and for a more accurate precision, two standards (one slightly above, and the other one slightly below the sample absorbances are used). Calibration is performed by using different standards starting with the blank solution (which in most cases is distilled water) to zero the instrument. The standards were analysed starting with the lowest in concentration and a blank run between the standards to ensure the baseline had not changed. It is advisable to dilute the samples if they are too concentrated and therefore beyond the concentration range.

Using GFAAS, calibration is done automatically depending on the programmed settings. However, in principle the procedure is the same as in FAAS described above.

Limit of detection and reproducibility in gold determination.

Limit of detection (l.o.d) is the lowest concentration that can be "reliably" detected. There are numerous definitions of this ill-defined quality. It can also be defined as the concentration of an element that gives a signal equal to twice the peak-to-peak noise level of the baseline (Harris, 1986).

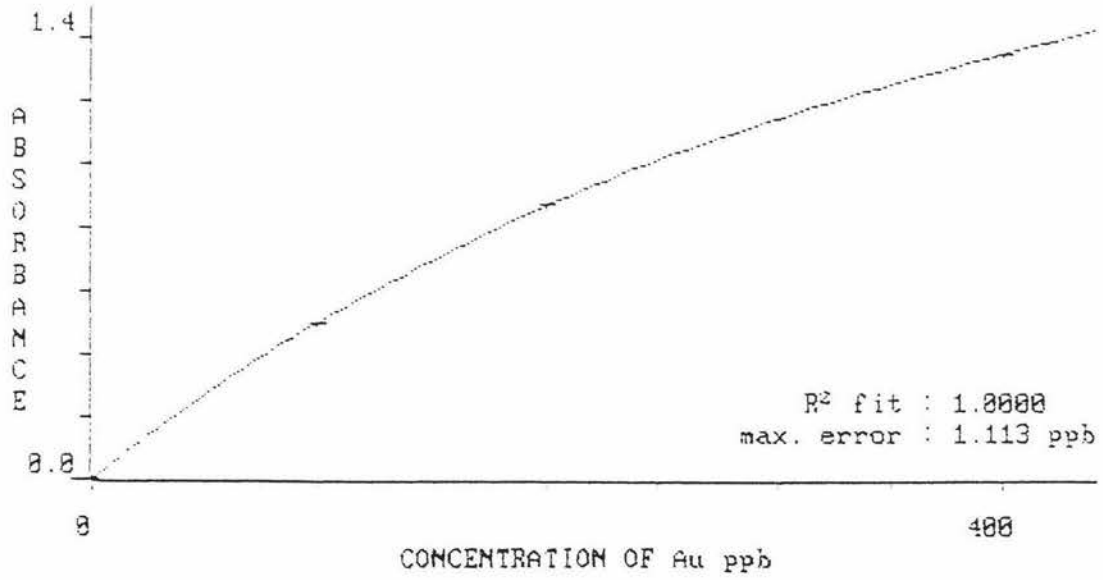


Figure 2.4. Calibration curve for gold showing absorbance vs concentration

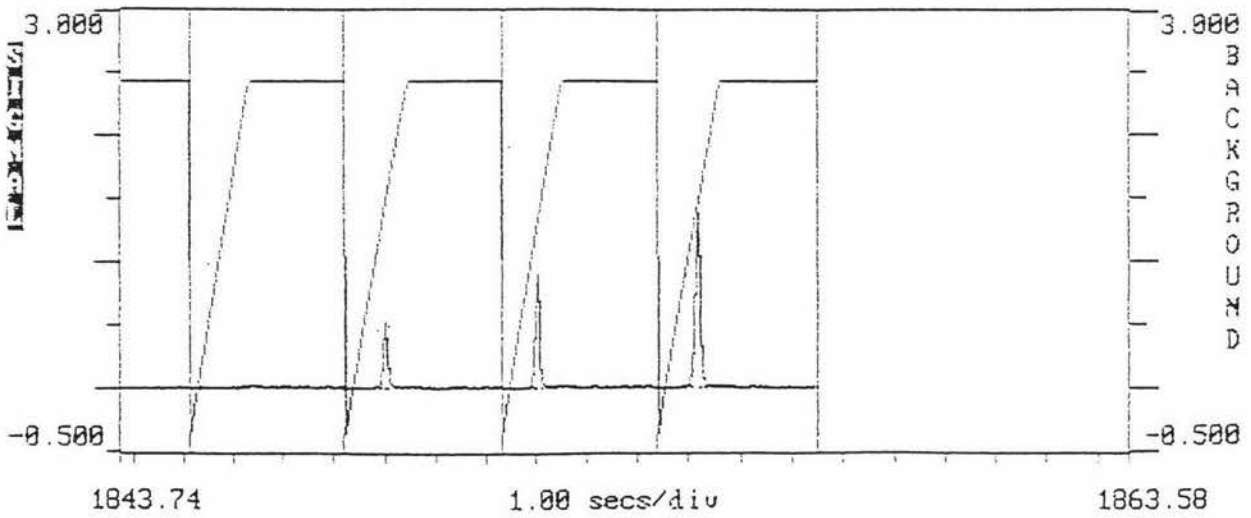


Figure 2.5. Peaks of different gold standards

Gold determination by GFAAS for this research had a nominal limit of detection (l.o.d) at 2σ, of 9 μg/L, or 4.5 mg/L at 1σ (σ is std. deviation). This calculation was made from visual examination of a threefold zoomed printout of an absorption peak of a sample containing 25 μg/L gold, estimating the standard deviation from this printout and then calculating the gold concentration that would give a peak 1σ or 2σ above the baseline. The reproducibility of the signal at 25 μg/L was calculated from 10 replicates and found to be 7.9%. A typical illustration of the measurement of the l.o.d. is shown in Figure 2.6.

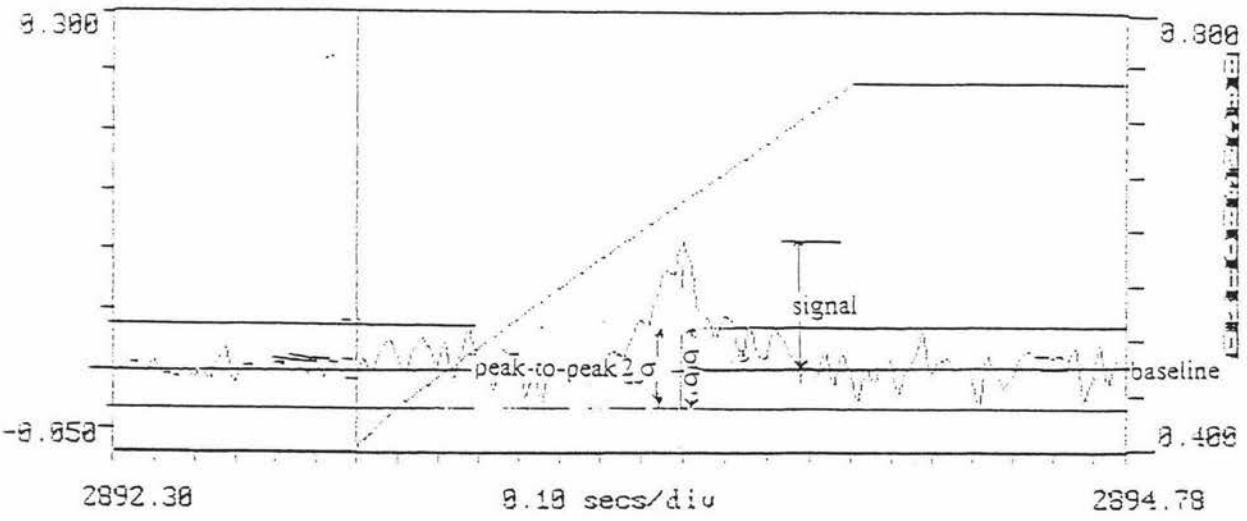


Figure 2.6. Illustration of the measurement of detection limit, peak-to-peak noise level and signal level. The signal is measured from its base at the midpoint of the noise component.

The above value for the l.o.d., referred to solutions (in MIBK or water) and did not relate to the original solid sample. It is possible, and indeed desirable, to extract the gold into MIBK as a chloro complex from a solution of a rock, soil or plant made from HCl or aqua regia. In such cases, where for example a 1 g sample could be dissolved in 20 mL of acid and extracted into 1 mL of MIBK, the l.o.d. (2σ) would be 9 μg/kg in the

original solid sample. The design of GFAAS also permits multiple loadings of the analyte solution so that the l.o.d. (2σ) of 9 μg/L could be reduced to <1 μg/L by use of 10 loadings.

2.2.3 Flameless atomic absorption spectrometry

Elemental mercury is very volatile and causes analytical problems, these can be solved by use of flameless atomic absorption spectrometry. Mercury has poor sensitivity when analysed in the flame. However, it can be detected by flameless atomic absorption spectrometry at concentrations as low as 0.001 mg/kg. For the purpose of this research, the l.o.d. was 0.01 mg/kg (see Figure 2.7).

In the above method, flameless atomic absorption spectrometry replaces the flame cell with a system in which groundstate atoms are either generated outside of the cell and are carried through with a carrier gas, or are generated in an enclosed space by means of an electric current. In the reduction-aeration technique, sample was dissolved in 0.5M HCl and mercury was reduced to the elemental state with the reducing agent sodium borohydride solution ($NaBH_4$). Mercury was then flushed out of the solution by bubbling nitrogen through the solution. The mercury vapour could now be swept into a glass tube aligned in the path of the atomic absorption spectrometry which absorbs the lines of mercury in a similar way as in a flame.

The apparatus used for the mercury determination consisted of a quartz cell positioned in the path of the emission from a hollow cathode lamp operating in a GBC909A atomic absorption spectrometer operating in the "flame" mode. Generation of the mercury vapour was effected by use of a Perkin Elmer MHS 10 hydride generation instrument.

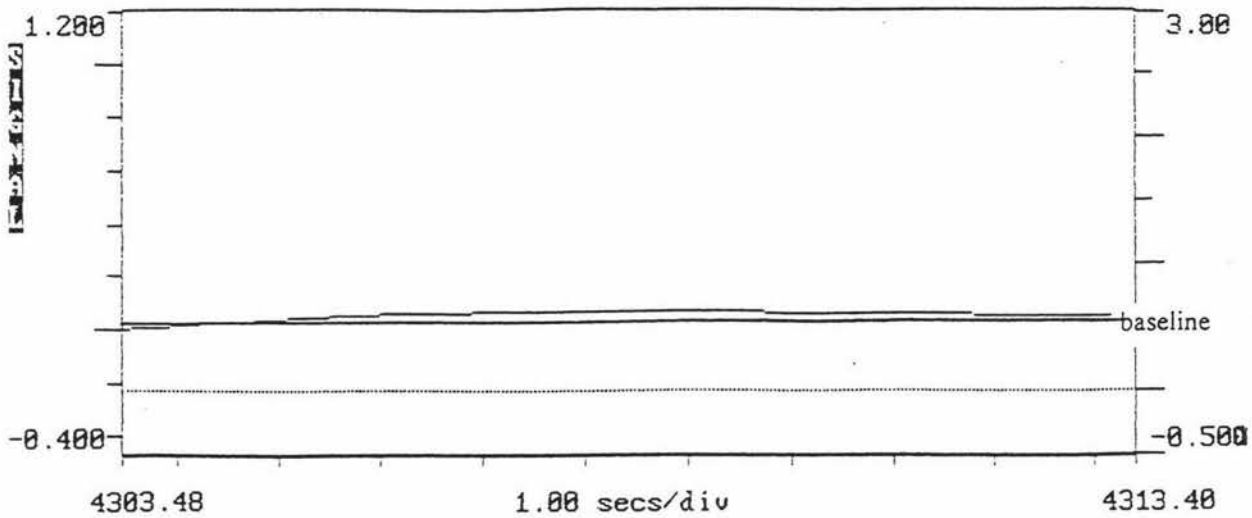


Figure 2.7. Illustration of limit of detection of mercury at 0.01 mg/kg.

The procedure for mercury determination in plants used in the experiment was based on Table 2.4 below.

Table 2.4. Application parameters for mercury test

Type	Application parameters
Application Name	Hg Msuya
Element	Hg
Lamp Current (mA)	3.0
Wavelength (nm)	253.7
Slit width (nm)	0.5
Sampling mode	Manual Sampling

The slope of the working curve was determined by taking different volumes from a prepared 10 µg/L standard. This was achieved by first starting with a blank or RO water then moving upward adding more volume of the standard. A typical signal of one of the absorbances is shown in Figure 2.8.

Once the slope was determined, concentration of samples could be determined by introducing a known volume of the sample manually to the flameless atomic absorption spectrometry after dissolving the sample with 10 mL of 0.5M HCl and mixing it with a reducing agent ($NaBH_4$).

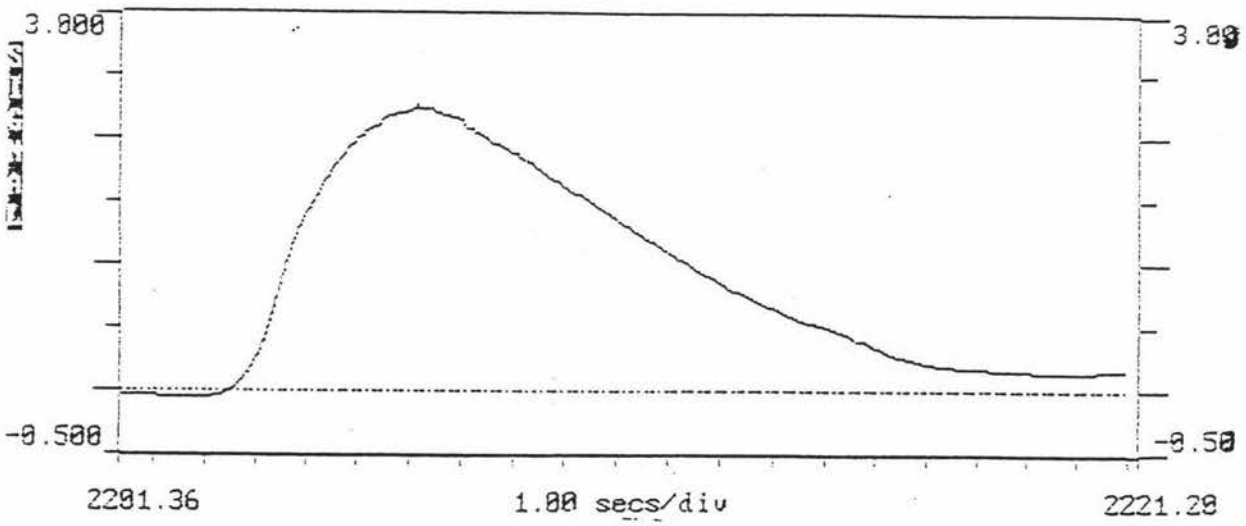


Figure 2.8. Typical illustration of mercury signal.

Reproducibility and limits of detection in mercury determination

The reproducibility of the mercury determinations was assessed as 8.6% after 10 replicate determinations of samples containing 1.0 mg/kg mercury.

The instrumentation for mercury analyses by flameless atomic absorption spectrometry depends on measurement of the absolute mass of mercury and it is thereby more difficult to assess the l.o.d. However, it was possible to detect down to 10 ng of mercury using the equipment described above. This approximated to 0.01 mg/kg (ppm) mercury in an original sample weighing 1 g as shown in Figure 2.8.

2.3 Sample preparation

2.3.1 Analysis of substrate

Generally gold is present in samples at a very low concentration and hence GFAAS is the best choice for metals which have a small concentration below the limit of detection of the FAAS. Interference of the absorption signal by iron is a common problem. Clarity of the signal was enhanced through selective extraction of a gold chloride complex into an organic phase. The solvent of choice for this research was methylisobutylketone (MIBK), after Brooks and Naidu (1985). At low molality, hydrochloric acid (ca 2M), K_d for gold in the organic phase is ca. 106, while iron is only very slightly absorbed from the aqueous phase (Kraus and Nelson, 1956). Cook (1998) established after exhaustive testing, the precision of this method using a GBC 3000 GFAAS instrument at Massey University."

Total gold

The method to be used in the sample-digestion procedure depends on the bulk geochemistry of an auriferous substrate. For this research, *aqua regia* was used. Samples were crushed and/or sieved and digested in the acid mixture through heating on a hotplate to almost dryness. The residual liquid was subsequently diluted with hydrochloric acid (2M), filtered and adjusted to a final volume with RO water. Aliquots were then extracted with MIBK and the organic phase analysed by GFAAS.

Extractable gold

Early experiments on uptake and translocation of gold by plants using thiocyanate by Shacklette *et al.* (1970), have opened up the way for further experiments on the use of thiocyanate on substrate to induce the uptake of the metal. Anderson (2000) reported several extraction systems to estimate the soluble fraction of gold in a substrate. It seems likely that the concentration of chemically soluble gold is proportional to induced plant uptake. In my research, the thiocyanate and thiosulphate extractions used by this author have been adopted.

To determine extractable gold, a crushed and sieved auriferous substrate (2 g) was weighed into a 50-mL polypropylene centrifuge tube. Ammonium thiocyanate solution (20 mL of 0.2 g/L) was added and the tube rotated in an end-over-end shaker for approximately 20 hours. Clear samples were analysed by GFAAS. Those which were turbid, were run for a short period in a centrifuge then filtered and analysed. Samples which showed low gold concentrations, were acidified with an equal volume of HCl (2M), extracted with MIBK and the organic phase analysed by GFAAS.

Similarly, thiosulphate (ammonium salt) was used as one of the extractants. In most cases, the ammonium, instead of the sodium, salt was used, as the latter (used in one experiment only) gives a large interference pattern from sodium. Thiosulphate solution could not be extracted into MIBK due to sulphur occlusion of gold that occurs as a function of acidification.

2.3.2 Determination of gold in plants

To determine the concentration of gold within plants for induced uptake experiments, samples were ashed overnight at 500°C and digested in *aqua regia*. After heating on a hotplate to almost dryness, RO water was added to adjust the mixture volume to 10 mL before analysis by FAAS or GFAAS. Later research work by Anderson (2000) indicated that digestion of the plant ash in aqua regia is not necessary. The quickest, cleanest and

most accurate method appears to be ashing overnight at 500°C, followed by dissolution of the ash in hydrochloric acid (2M) Anderson (2000).

2.3.3 Determination of mercury in plants

Determination of mercury in plants differs to some extent to the procedure of gold determination above. In mercury determination, the sample was digested in 10 mL of concentrated nitric acid. After heating on a hot plate to almost dryness, RO water was added to bring up the volume to 10 mL before analysing by flameless atomic absorption spectrometry. For mercury determination, plant samples were not ashed.

CHAPTER 3 - METAL LEACHING OF TUI MINE TAILINGS AND ITS SIGNIFICANCE FOR THE ENVIRONMENT AND PHYTOMINING FOR GOLD

3.1 Introduction

The sulphide-bearing minerals of most global base-metal deposits generate acid as a product of natural weathering. Where large volumes of sulphide ore is exposed to the atmosphere, sulphide oxidation and production of metal-contaminated drainage eventuates. Geochemical processes control the evolution of low pH from oxidation of pyrite in the presence of oxygen and water. The low pH facilitates the growth of bacteria and mobility of toxic metals (arsenic, copper, cadmium, lead and zinc) which eventually find their way as runoff or leachates into the environment.

Acid mine drainage (AMD) caused by weathering and oxidation of waste rock and mine tailings from the Tui base-metal mine, has generated what is perhaps the most severely metal-polluted environment in New Zealand. Liberation of metals to the environment depends on the weathering processes. Tui tailings are auriferous and contain up to 1.0 mg/kg (1 ppm) gold. Gold appears in association with chalcophile metals (defined as metals having a high affinity for sulphur) such as lead, arsenic, cadmium, copper and zinc. Since the closure of the mine in 1974, the tailings have been left to weather. Pyrite (FeS_2) oxidation has lead to AMD polluting streams, rivers and sediments (Morrell, 1997). It is important to note that in the undisturbed environment, *in situ*, sulphide minerals are primarily found mostly beneath the water table. Under these natural conditions, contact of sulphide minerals with oxygen is minimised by the overlying soil and groundwater and the oxidation process is almost negligible. However, once the cover has been exposed by activities such as mining, large quantities of sulphide-containing rock become vulnerable to weathering and accelerated sulphide oxidation, resulting in high acid generation.

The oxidation of pyrite is a complex reaction, which includes a series of oxidation-reduction reactions, complex ion formation, hydrolysis, solubility controls and kinetic effects. In an oxidising environment, pyrite reacts with oxygen and water to form soluble iron, as well as free sulphate and acid according to the following equation:

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

Non-ferrous sulphides (galena and sphalerite), also undergo oxidation, but acid is not generated during the reaction (Morrell, 1997).

$$MS + 2O_2 \rightarrow MSO_4 \text{ where: M = Zn, Pb, Ni etc}$$

Within the Tui tailings, lead is oxidised to anglesite ($PbSO_4$), while the high solubility of $ZnSO_4$ leads to leaching of this metal.

3.2 Aim of the experiment

The aim of the experiment described in this chapter was to find the most suitable leachant to be used for phytomining of gold while at the same time minimising release of other toxic metals.

3.3 Materials and Methods

Environmental effects of induced phytomining are centred on two main problems: the actual toxicity of the reagents used, and the toxicity of heavy metals released by these chemicals. A series of experiments were carried out in which columns containing several sulphide affinity heavy metals were amended with lime to give various pH values and were leached with ammonium thiocyanate, ammonium thiosulphate and water. The concentrations of gold, copper, cadmium, zinc and lead were determined in these leachates and conclusions made about the relative rates of leaching of gold and

heavy metals therefrom. Whether water, thiocyanate or thiosulphate will be used for phytomining for gold will depend on the extent to which heavy metals, other than gold, are leached from the tailings. Ammonium thiocyanate has a toxicity of over 200 times less than that of cyanide and is graded 3 on the toxicity class. Ammonium thiosulphate is over 1000 times less toxic than cyanide and is degraded quickly to class 5 sulphate

3.3.1 Design for leaching experiments

Tailings material was crushed and sieved to <0.5 mm, and mixed with different amounts of lime (0.1%, 0.2% and 0.3% $CaCO_3$). Material (600 g) was packed in each of 12 polypropylene columns measuring 250 mm in length and 50 mm internal diameter comprising of 3 sets. In each set, there were four columns marked "0%, 0.1%, 0.2% and 0.3% lime." The first set of columns was leached with RO water, the second with 2 g/L thiocyanate and the third set with 2 g/L thiosulphate solution of pH 6.9, 6.4 and 6.6 respectively. The bottom of each column was covered with 0.1 mm nylon gauze (Figure3.1). One hundred and fifty millilitres of solution was first applied to the columns to saturate the tailings materials. Subsequently, 50 mL of solution was added each day for 7 days and the leachates collected.

In a second experiment, Tui tailings material unamended with lime was packed into 250 mm columns and leached with thiocyanate at several concentration levels 1.0g/L, 5 g/L, 7.5g/L and 10 g/L. As in the first experiment, the solutions were passed at the rate of 50 mL/day after an initial saturation of 150mL.

In a third experiment, small columns (120x15 mm) were packed with 80g of crushed and sieved (<0.5 mm) Tui tailings containing admixtures of calcium carbonate: 0.0 (control), 0.02%, 0.04%, 0.06%, 0.09%, 0.125% and 0.5%. Columns were charged with 50 mL of thiocyanate, thiosulphate or water and repeated with 20 mL of solution each day for seven days. Leachates were collected daily and stored at 4^0C before analysis.

3.3.2 Chemical analysis of leachates

Each daily leachate was measured for pH and analysed for gold, cadmium, copper, lead and zinc by flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS) as described earlier in Chapter 2.

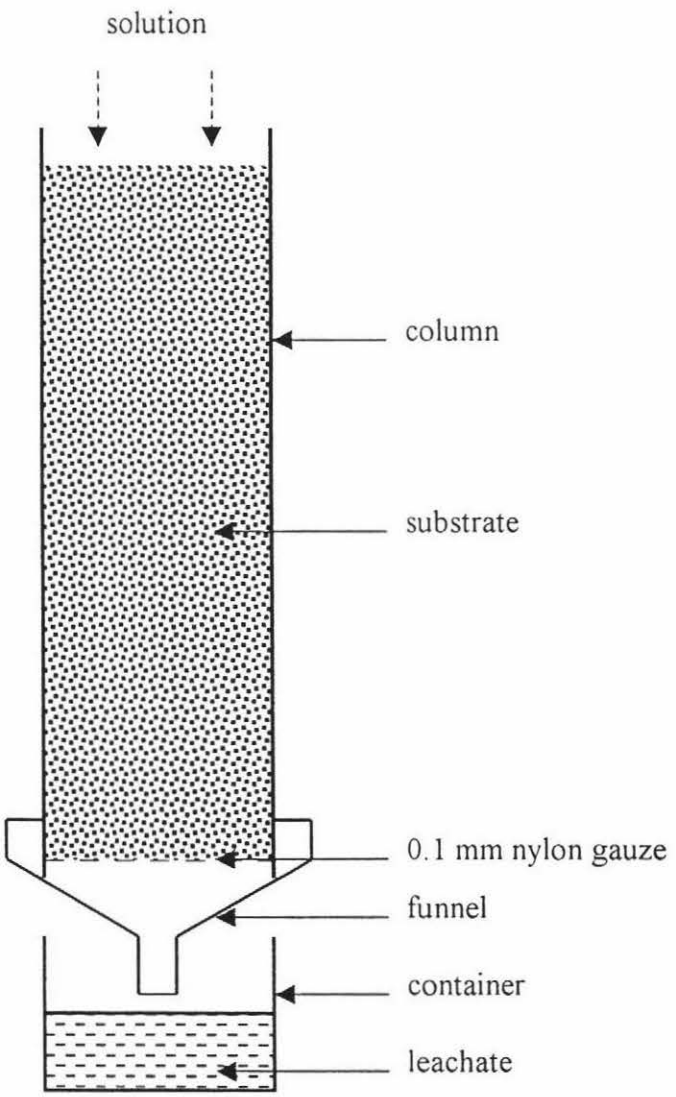


Figure 3.1. Schematic diagram of the leaching column

3.4 Results and Discussion

The gold concentrations in the Tui mine tailings range from 0.5 to 1.0 mg/kg (ppm). Anderson *et al.* (1998), were able to extract 22.6% of the total gold from 1 g of Tui mine tailings into 10 mL of 2 g/L ammonium thiocyanate solution. They compared four gold ores and the amount of their extractable gold (Table 3.1). They concluded that the ores with the greatest extractable gold were acidic sulphide mine tailings which also had the lowest total gold concentrations but contained heavily weathered residual gold. The point to note here is that it is the geochemistry of the soil or substrate that finally determines extractability of the contained metals. Despite the fact that ores such as Macrane ore or Waihi mine ore had higher total gold than Tui mine tailings, they had the lowest extractable gold.

Table 3.1. Thiocyanate-extractable gold in different types of mineralised substrate

Substrate	Ore geochemistry	Total Au(μg/g)	Extractable Au(ng) in 1 g of tailings	% Total Au extractable*
Waihi mine[+]	Native Au	3.45	61.6	1.78
Tui mine[□]	Acid sulphides	0.56	114.8	22.60
Macrane mine[π]	Reduced Au ore	4.63	27.7	0.60
Artificial ore[♥]	Disseminated Au	5.00	460.9	9.20

* Percentage of total Au extractable in 24 hours in a 1:10 substrate:water ratio by 2 g/L ammonium thiocyanate in 24 hour.
[+] Coromandel, New Zealand
[□] Te Aroha, New Zealand
[π] Macraes Gold Mine, Central Otago, New Zealand
[♥] Finely disseminated gold prepared by adding gold chloride to quartz sand and heating to convert to native gold.
Source: (Anderson 2000)

3.4.1 Extraction from unlimed tailings: low pH

Use of thiocyanate

Plots of cumulative extraction of gold, zinc, copper, lead, and cadmium using ammonium thiocyanate in unlimed columns over a 7-day period are shown in Figure 3.4. The extraction pattern shows the effectiveness of thiocyanate as an extractant for gold. It is clear from Figure 3.4 that, thiocyanate is far more selective for gold than for the other metals. The disproportionality of gold extraction to the other metals is very high (x15), which enhances thiocyanate value as an extractant specific for gold. Table 3.2 shows that 4.28% of the total gold was removed from the tailings which had a low pH of 2.7 after treatment with 350 mL of 0.2 g/L of thiocyanate. However, at higher pH, only 2.24% of the gold was removed. This therefore means that the extraction of gold by thiocyanate is strongly pH dependent. A different experiment undertaken by Anderson, 2000 (unpublished) emphasises this point. This author collected 12 samples of Tui from different points on the tailings dump and extracted each with thiocyanate. From Figure 3.2, which shows his results, it can be seen that there is a big variation of pH in the Tui tailings and the use of ammonium thiocyanate solution on gold is a function of pH.

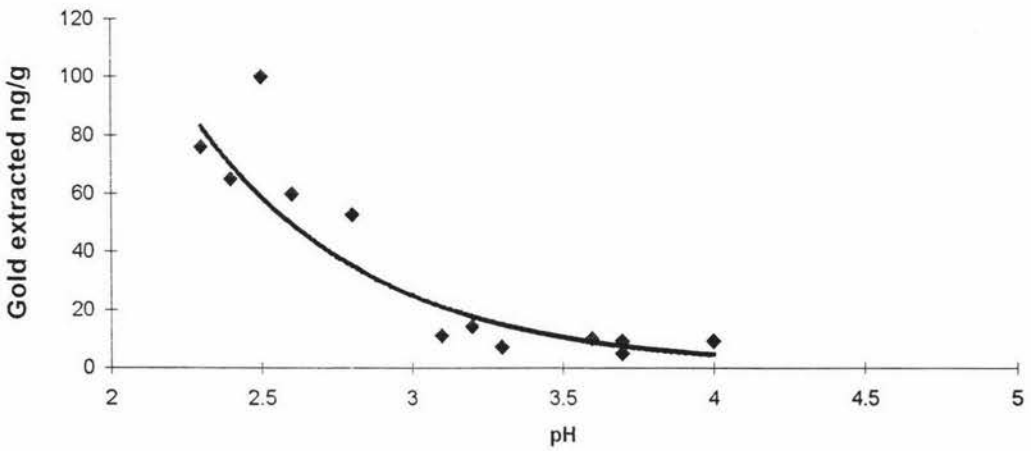


Figure 3.2. Gold extraction from Tui mine (wet) tailings using 2 g/L thiocyanate at different pH sampling sites

Table 3.2. Percentages of metals removed from Tui tailings after a 7-day leaching with various reagents.

	Gold	Cadmium	Copper	Lead	Zinc
Original concentration	0.7 mg/kg	27 mg/kg	4600 mg	1.15%	5400 mg/kg
Without lime					
Thiocyanate leaching	4.28%	0.63%	0.11%	0.02%	0.04%
Thiosulphate leaching	0.11%	0.52%	0.02%	0.01%	0.11%
Water leaching	<0.01%	<0.01%	<0.01%	<0.01%	0.14%
With 0.3% lime					
Thiocyanate leaching	2.24%	0.01%	<0.01%	<0.01%	0.03%
Thiosulphate leaching	0.06%	0.11%	0.01%	<0.01%	<0.01%
Water leaching	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%

Use of RO water

Plots of cumulative concentration (at substrate pH of 2.7) of zinc, copper, lead, cadmium and gold using RO water are presented in Figure 3.3. Zinc shows higher mobility in water at this pH range than the other elements followed by copper. Zinc, which may have undergone oxidation to form zinc sulphate, was easily eluted by water (about 8000 μg). Other metals were also leached out by water in the order of Zn<Cu<Pb<Cd. Gold was not eluted by water because of its low solubility.

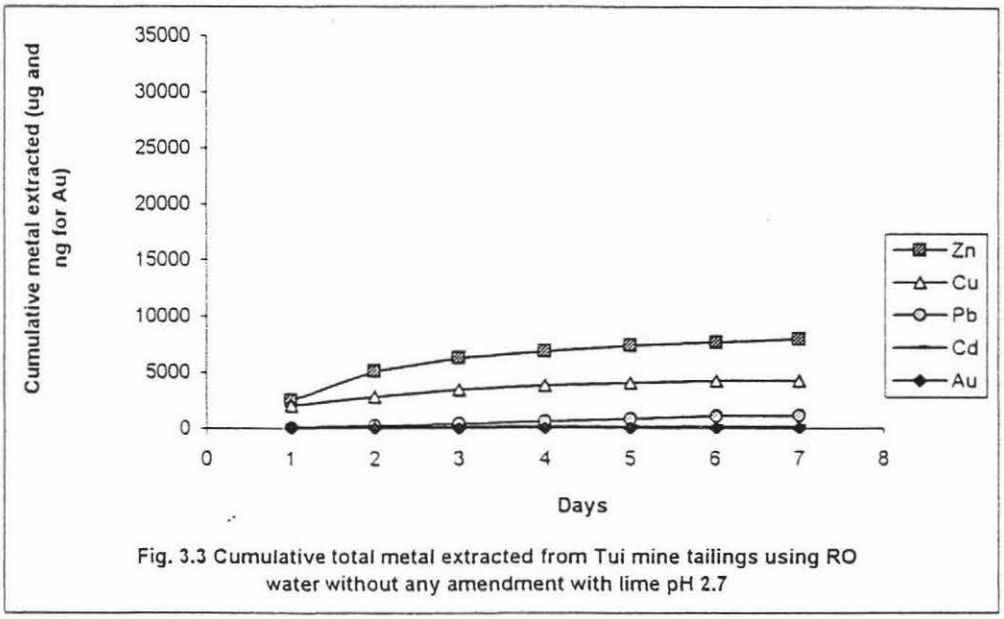


Fig. 3.3 Cumulative total metal extracted from Tui mine tailings using RO water without any amendment with lime pH 2.7

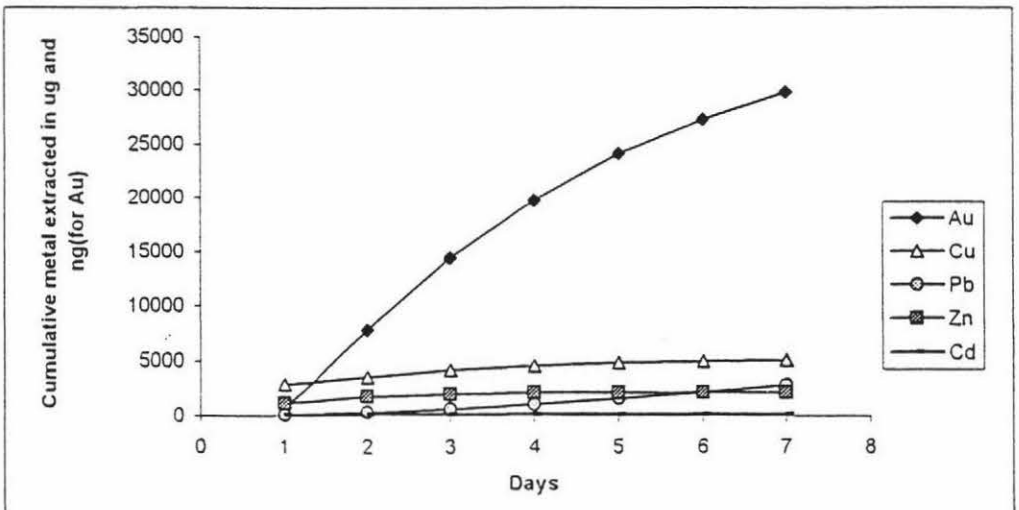


Fig. 3.4 Cumulative metal extracted from Tui mine tailings using 2 g/L CNS

Concentration of base-metal leached by thiocyanate and RO water are very similar (see Figures 3.3 and 3.4). It is probable that leaching of base metals from the Tui mine tailings is a function of the natural pH. Only gold is leached by complexation with thiocyanate.

Use of thiosulphate

Fig 3.5 shows the plots of extraction of zinc, copper, lead, gold and cadmium using 2 g/L ammonium thiosulphate, with no lime added, and at a pH of 2.7. From the results of the experiment it can clearly be seen that there is suppression of the amount of zinc removed (6000 μg) as compared with using water (8500 μg). However, mobility of zinc in thiosulphate was higher than the other metals. Gold extraction is about 30 times less than when using thiocyanate at the same pH. The plot shows some reaction, but the pH may be too low to inhibit effective removal of gold using thiosulphate and therefore complexation of gold. Anderson (2000) has proposed that at low pH, thiosulphate solution is destabilised leading to poor metal complexation.

From the results of the two solutions used (thiocyanate and thiosulphate), thiocyanate is the best reagent for the removal of gold at low pH compared to thiosulphate

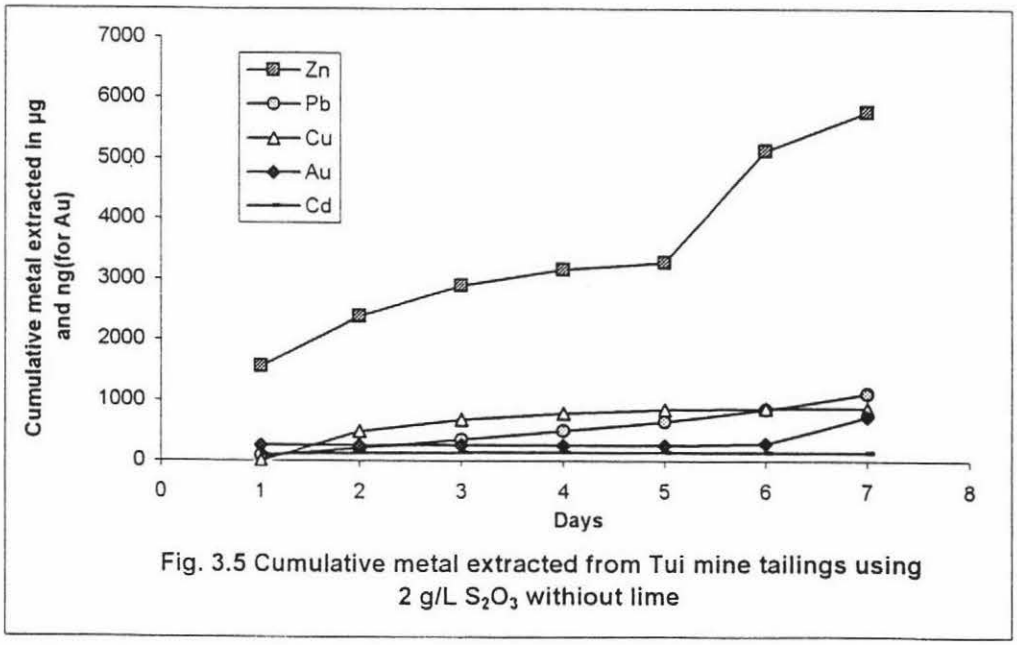


Fig. 3.5 Cumulative metal extracted from Tui mine tailings using 2 g/L S_2O_3 withiout lime

3.4.2 Extraction from limed tailings (at 0.3%lime)

Use of RO water

Using water at a lime rate of 0.1%, the pH of the substrate was also 6.9. Zinc, which was more mobile at low pH, became less mobile (3500 μg). Further increase of lime to 0.3% raised the pH to 7.3 and zinc leaching was suppressed to 500 μg (Figure 3.6). The solution concentrations of other metals were also suppressed. This implies that weathering/leaching of metals *in situ* in a sulphide ore is higher in an acidic environment. This emphasises the conclusion that leaching of metals is a function of low pH.

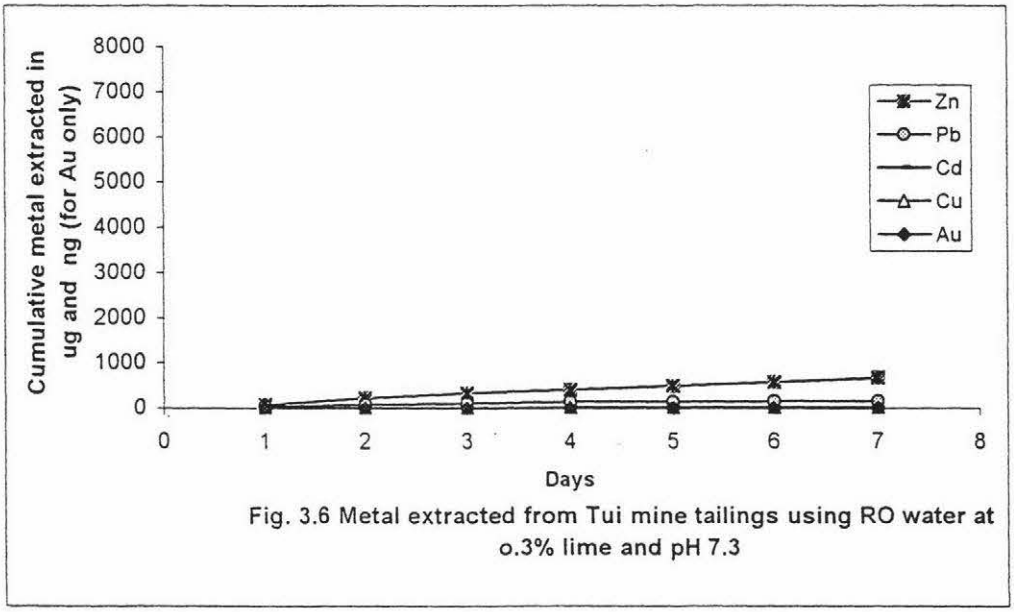


Fig. 3.6 Metal extracted from Tui mine tailings using RO water at o.3% lime and pH 7.3

Use of thiocyanate

Figure 3.7 shows plots of cumulative extraction of gold, zinc, lead, copper and cadmium for a lime addition of 0.3%, (pH 7.7). Aqueous extraction of gold was reduced to almost a half (16000 ng) as compared to 29,800 ng when lime was not added (see Figure 3.4). Gold extraction remained much higher relative to the other base metals, suggesting again that only gold was complexed by thiocyanate.

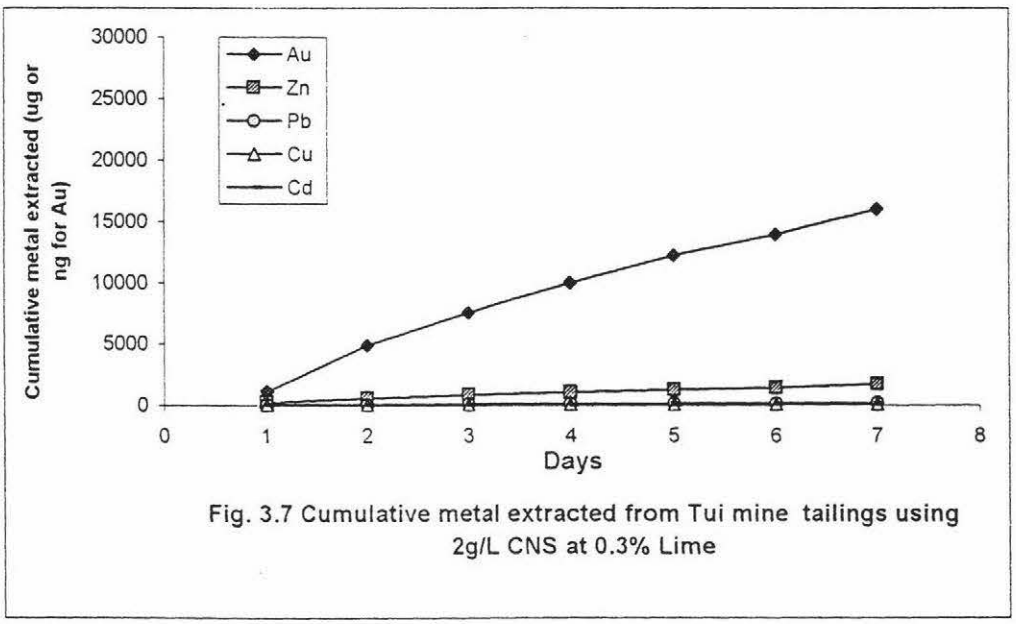


Fig. 3.7 Cumulative metal extracted from Tui mine tailings using 2g/L CNS at 0.3% Lime

Use of thiosulphate

Figure 3.8 shows plots of cumulative extraction of metals using 2 g/L thiosulphate solution at a lime rate of 0.3%. At high pH, zinc becomes almost totally insoluble (40 μg). This observation again supports the conclusion that leaching of metals is a function of low pH, there is no significant evidence of base-metal complexation with thiosulphate. From Figures 3.5 and 3.8, the pattern shows that gold extraction was reduced by almost a half (736 to 416 ng).

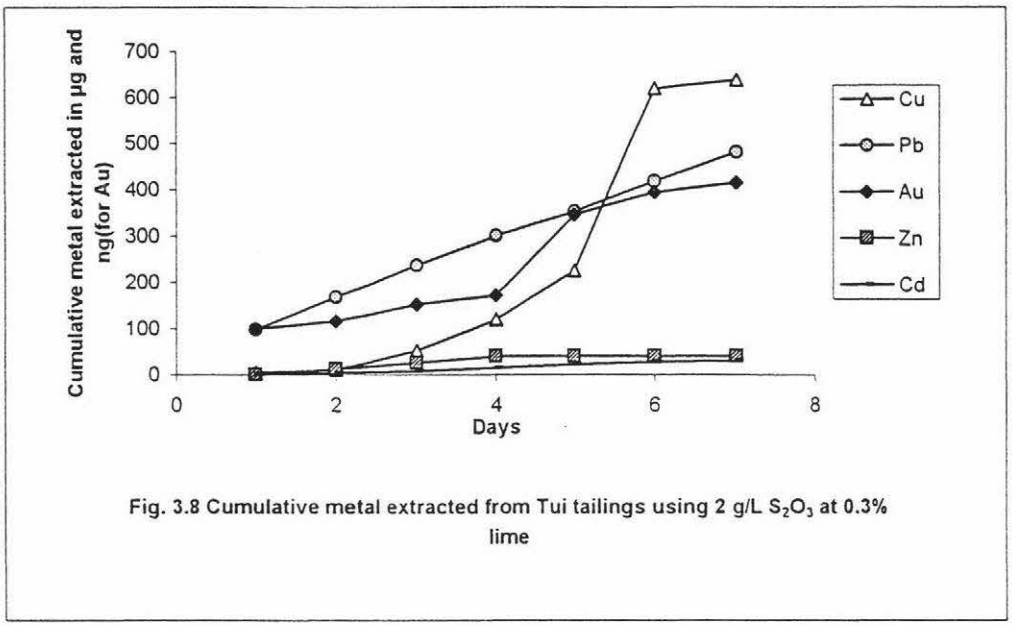


Fig. 3.8 Cumulative metal extracted from Tui tailings using 2 g/L S_2O_3 at 0.3% lime

3.4.3 Enhancement of extraction by use of increasing concentrations of thiocyanate and thiosulphate

Use of thiocyanate

The effect of increasing the concentration of the thiocyanate elutant on the extractability of gold is shown in Figure 3.9. It can clearly be seen from the plots that extraction of gold increased linearly with the concentration of thiocyanate. There is limited evidence for any base-metal complexation with thiocyanate, even at a high salt concentration.

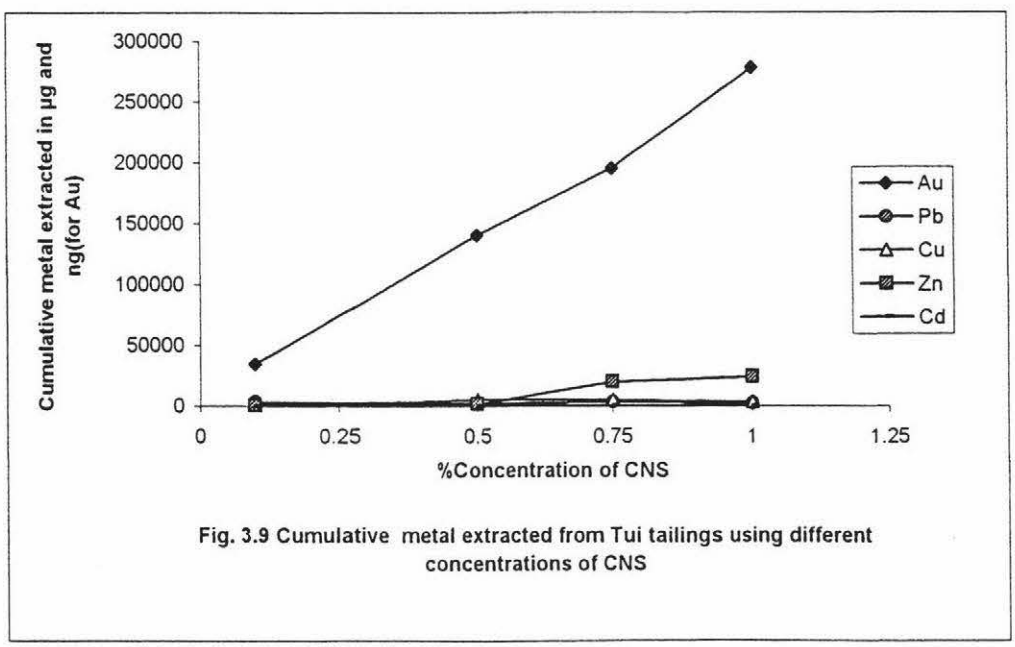


Fig. 3.9 Cumulative metal extracted from Tui tailings using different concentrations of CNS

Use of thiosulphate

Plots of increase in concentration of sodium thiosulphate from 0.1 to 1.0% (1 g/L to 10 g/L) are shown in Figure 3.10. Only zinc could be extracted at this low pH (4) and concentration (<0.25%). With increase in concentration of thiosulphate, only lead and gold showed significant increases in extractability. At higher concentration of thiosulphate there is evidence for complexation with lead and gold, but not with zinc, copper and cadmium.

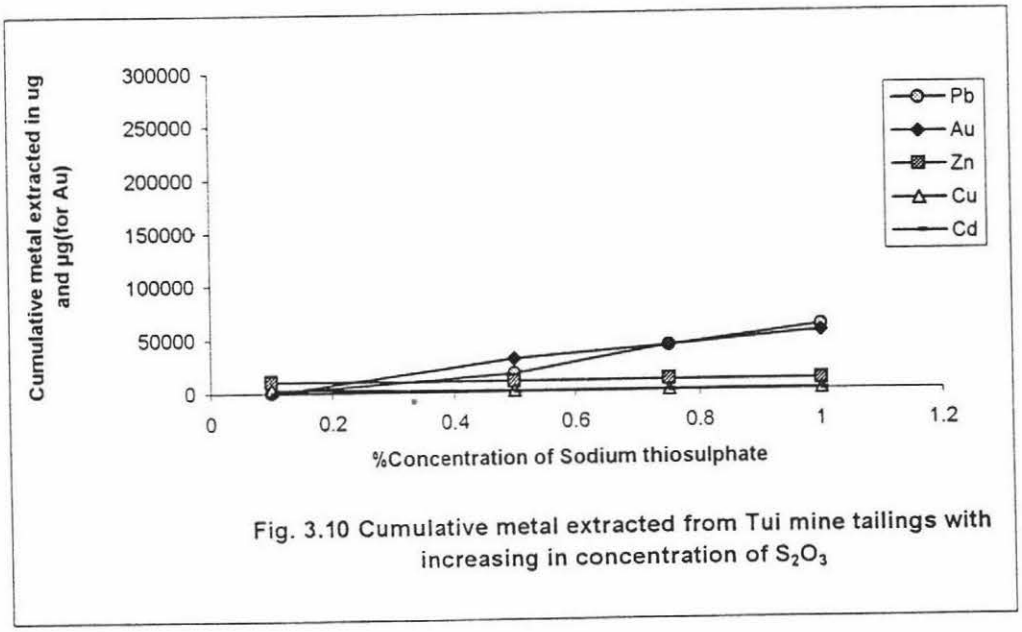


Fig. 3.10 Cumulative metal extracted from Tui mine tailings with increasing in concentration of S_2O_3

3.4.4 Extraction behaviour of thiocyanate and thiosulphate over a range of pH

Extraction behaviour using thiocyanate

Plots of extraction of gold over the pH range of 3.1, 4.4, 6.3, 6.7 and 7.0 using small columns are shown in Figure 3.11. Using thiocyanate, there was a general trend of decreasing extraction of all the metals as a function of increasing pH. The decrease was more noticeable at pH 6.3.

Extraction behaviour using thiosulphate

Plots for metal extractions using 2 g/L ammonium thiosulphate at pH 4.2, 5.8, 6.7, 7.0, 7.4 and 7.7 using small columns are shown in Figure 3.12. Low pH results in more lead

being leached out especially at pH <4.2 (>8000 μg). Other metals at that pH are almost ten times less leachable than lead. However, at the higher pH of>7.7, gold is eluted more than the other metals and lead almost disappears altogether. At this point it would probably be a good idea to increase the pH further (say to 9) and find the optimum pH value for gold extraction using a thiosulphate solution. I am not sure why the concentration of lead with thiosulphate at low pH is so high. It is unlikely that thiosulphate complexation is responsible for this anomaly due to the instability of thiosulphate in acidic media. Perhaps a sulphate, generated by the degradation of thiosulphate, increased lead solubility at low pH.

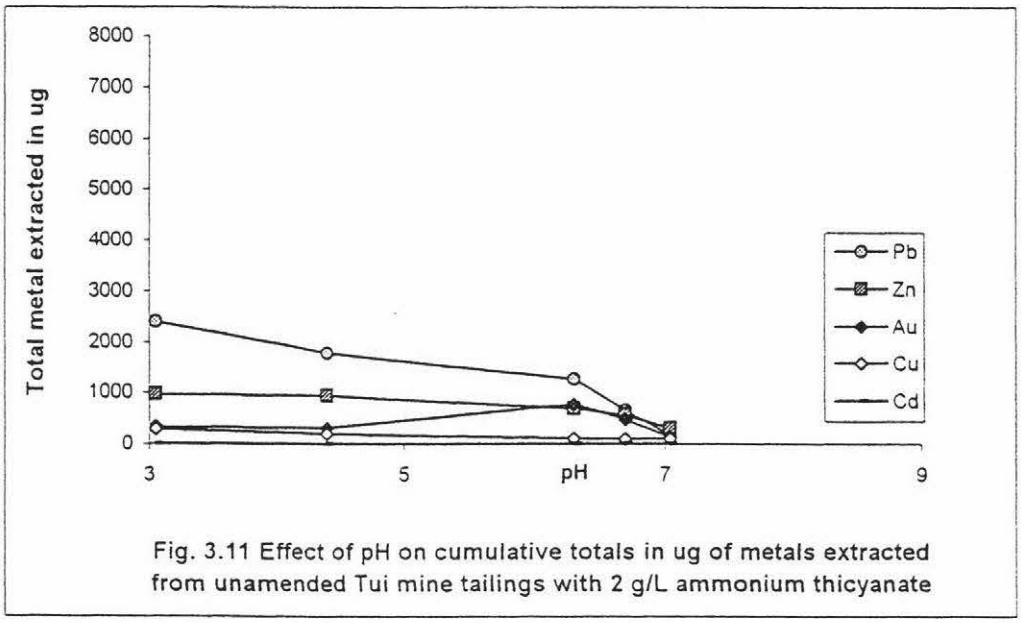
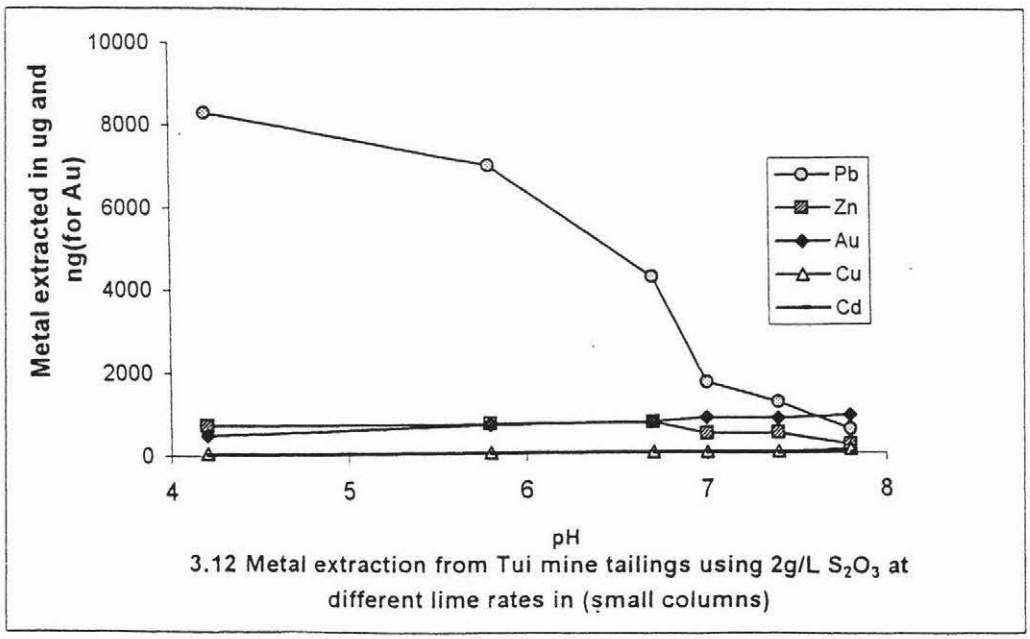


Fig. 3.11 Effect of pH on cumulative totals in ug of metals extracted from unamended Tui mine tailings with 2 g/L ammonium thicyanate



3.12 Metal extraction from Tui mine tailings using 2g/L S_2O_3 at different lime rates in (small columns)

3.5 Conclusions

The following conclusions can be made regarding the use of ammonium thiocyanate, thiosulphate or water for phytomining of gold and the secondary effects manifested by other chalcophile metals.

1. Under acid conditions, leaching of base metals from the Tui tailings was a function of the low pH. Ammonium thiocyanate was highly selective for gold at pH 4, but relative to water did not increase the solubility of the other metals studied. This indicates that under acidic conditions, thiocyanate only forms a soluble metal complex with gold. At a similar pH (4.2), thiosulphate increased the solubility of zinc but showed poor complexation with gold.

2. The amount of gold extracted at acidic pH increased in direct proportion to the thiocyanate concentration applied to the substrate.

3. At higher pH values, thiocyanate remained selective for gold, but removed about 50% of the amount extracted at low pH. The increased concentration of gold extracted by thiosulphate at higher pH indicates that a gold-thiosulphate complexes forms under alkaline conditions.

4. The general trend observed was that for thiocyanate in the pH range 3.2 to 7.0, there was a tendency to decreasing extraction of gold and base metals as the pH increased. For this same pH increase, thiosulphate showed a slight increase in removal of gold but a large decrease in lead extraction. Thiocyanate was more effective in removing gold than thiosulphate at all pH values, and particularly at low pH.

This study has shown that thiocyanate is a prime solubilising agent for gold in phytomining operations. This suitability is linked to the selectivity of this reagent for gold compared with the chalcophile elements, cadmium, copper, lead and zinc. Leaching of other metals appears to be a function of low pH and not complexation with thiocyanate.

CHAPTER 4 - CHEMICALLY INDUCED GOLD UPTAKE BY ROOT CROPS FOR THE PURPOSE OF PHYTOMINING

4.1 Introduction

Successful work undertaken by Shacklette *et al.*, (1970) who reported the uptake of gold by plants from hydroponic solutions of gold, has created further interests on the subject. They grew unrooted cuttings of *Impatiens* spp. in solutions of gold chloride, cyanide, bromide, iodide, thiocyanate and thiosulphate for 48 hours. Passive uptake of gold was apparent for all of the solutions used. Using this research as a stating point, Anderson *et al.* (1998) induced uptake of gold up to 57 mg/kg in dried leaves of *Brassica juncea* and proposed that it could be technically feasible to grow 'a crop of gold' using *Brassica juncea* or other plant species to carry out phytomining for gold in mine tailings. This was a great step forward as research jumped from hydroponic to solid substrates.

4.2 Aim of the experiment

The aim of the experiment described in this chapter was to find out whether gold concentration in roots was higher than in the shoots and to find the possibility of using root crops for phytomining for gold.

4.3 Materials and Methods

4.3.1 Plants

Root plants were selected for this experiment because various researchers have reported greater accumulation of metals in roots relative to aerial organs. The following plants were selected for the experiments: *Raphanus sativus* 'oriental radish' and 'salad

radish', *Beta vulgaris* 'Derwent globe', *Allium cepa* 'Pukekohe longkeeper', and *Daucus carota* 'topweight carrot'. The seeds were initially sown in standard commercial seed-raising compost and then transplanted into the auriferous substrate after the first pair of true leaves had appeared.

4.3.2 Auriferous Substrate

Plants were grown in artificial gold ore, containing 3.8 mg/kg gold in a mixture of (<2 mm) sieved pumice and silica sand.'Osmocote' slow release (4-5 months) fertiliser was then added to the substrate at the rates recommended by the manufacturer.

4.3.3 Plant Growth Experiments

Plants (17 radish, 13 beetroots, 11 oriental, 9 carrots and 9 onions) in varying replicates (out of which 9 were controls) were selected for this experiment. Each of three treatments (controls, thiocyanate, and thiosulphate), involved growth for 9 weeks in 250 mL or 500 mL plastic pots (depending on the anticipated root size of the plant) in a greenhouse maintained at 20-25°C and with random changing of pot positions to ensure consistency of illumination. At the end of the growing period, solutions of ammonium thiocyanate or ammonium thiosulphate were applied to the substrates at rates of 1.0 g/kg of thiocyanate and 2.0 g/kg of thiosulphate respectively. After a period of 10 days, the thiocyanate-treated plants had died though those treated with thiosulphate still had viability (see Plate 4.1). The plant material was then harvested and dried at 70°C.

4.4 Chemical Analysis

Dried plant samples (ca. 0.5 g) were ignited at 500°C in borosilicate test tubes and the ash heated over a hot plate with 5 mL of aqua regia until the volume had been reduced to about 1 mL. The residues were subsequently diluted to 10 mL with deionised water and analysed for gold using a GBC 909 atomic absorption spectrometer capable of

Plate 4.1 **Different root plants 10 days after treatment with ammonium thiocyanate and ammonium thiosulphate**

Plate 4.2 ***Brassica juncea*** **species in flower before treatment**

determining down to 0.5 mg/L (ppm) gold in the solution. For gold concentrations lower than 0.5 mg/L, 4 mL aliquots of the aqueous solution were shaken with 2 mL of methylisobutylketone (MIBK) and the organic layer analysed for gold by graphite furnace atomic absorption spectrometry (GFAAS) as described in Chapter 2.

4.5 Results and Discussion

Concentrations of gold in above-ground parts and roots of the five vegetables used, are given in Table 4.1. Values in some cases exceeded 200 mg/kg and were much higher than the maximum of 57 mg/kg reported for *Brassica juncea* by Anderson *et al.* (1998). Concentrations were in most cases higher in roots than in aerial plant parts. The controls showed no measurable uptake of gold (i.e. <5 μg/kg [ppb]) thus confirming the presence of gold in the substrate in an immobile form before chemical treatment. In terms of the mean gold concentrations of plants treated with thiocyanate, roots of nearly all species contained significantly more gold than the tops and in descending order can be ranked as: salad radish > oriental radish > carrot > onion > red beet.

Thiosulphate addition produced results comparable with those obtained with thiocyanate. In descending order the gold values in roots were: carrots > red beet > onions.

The final column of Table 4.1 shows the expected gold yield in g/ha for a root crop assuming that yields would be the same as for a commercial crop grown under optimum conditions. Such ideal conditions are not likely to be achieved under practical conditions in the field, especially over sterile mine tailings, possibly of low pH. Nevertheless, this expected yield has been retained in calculations of the anticipated economics of the system, because the allowance for costs of the chemicals was based on the use of 1 g/kg for thiocyanate and 2 g/kg for thiosulphate. It has been shown Anderson *et al.* (1998) that optimum gold yields could be obtained with a loading of 0.62 g/kg when using thiocyanate. The allowance of $US6950/ha for agronomic, incineration, and chemical costs is based on the following calculation:

Growing and harvesting a hectare of land providing 18 t/ha of carrots	- $2000
Cost of chemicals	- $2250
Incineration of the crop at $150 per tonne	-$2700
Total	-$6950

Table 4.1. Gold concentrations (mg/kg dry weight) in roots crops grown in a substrate with 3.8 mg/kg gold

Plant or treatment	Yield (t/ha)*	N	Mean	Std. dev.	Highest Au	% of total Au	Gold yield (g/ha)**
THIOCYANATE							
Carrot tops	2	2	3.16	0.06	3.21	19	6
Carrot roots	16	2	48.3	46.6	81.2	81	773 (779)
Onion tops	2	3	12.0	11.6	27.2	41	24
Onion roots	10	3	13.8	10.9	24.6	59	138 (162)
Red beet tops	3	4	6.50	2.10	10.3	35	20
Red beet roots	11	4	5.00	3.70	9.05	65	55 (75)
Salad radish tops	1	15	10.6	10.2	28.3	12	11
Salad radish roots	2	15	113	27.4	220	88	226 (237)
Oriental radish tops	1	9	5.00	4.90	14.3	7	5
Oriental radish roots	2	9	102	100	162	93	204 (209)
THIOSULPHATE							
Carrot tops	2	4	12.9	3.00	15.9	31	26
Carrot roots	16	4	89.0	74.0	189	69	1424 (1450)
Onion tops	2	3	21.5	13.4	35.8	76	43
Onion roots	10	3	2.60	2.10	4.30	24	26 (69)
Red beet tops	3	6	4.10	1.30	5.04	71	12
Red beet roots	11	6	3.20	1.00	4.72	29	35 (47)

* Source: Clarke *et al.* (1986) and based on wet weight.
** Values in parentheses are the totals of tops and roots.

The above calculation does not include the cost of recovering the gold metal from the plant ash. However, neither does it include the potential dividend from possible energy recovery from the incineration process itself. Such an idea is not fanciful and indeed in Queensland, electricity is routinely sold to the National Grid after incineration of the *bagasse* residue from the sugar processing industry. Current research experimenting on different ways of removing gold from plant material is under investigation and it is anticipated that sooner or later the true cost of the final process in phytomining to gold will be established.

More detailed calculations of the economics of phytomining for gold are given in Table 4.2 , from which it is clear that of the 5 root crops studied, only carrot is likely to provide an economic return for phytomining. Although the higher return would appear to be possible with the use of thiosulphate as an inducing agent, from experience (see Chapter 3 Fig. 3.5, that gold extraction does not occur at lower pH values when this reagent is used), it may be necessary to carry out the additional expense of liming. Some mine tailings have a pH well below 7.0 and it is difficult to grow plants at pH <4.0. For the more acid tailings additional liming (for plant growth) will be necessary even if thiocyanate is to be used.

The anticipated return of $840/ha for gold recovery with thiocyanate use is over double the return for a crop of wheat in the USA at current world prices.

Environmental concerns have to be addressed if chemicals are to be added to the soil. Despite their name similarity to cyanide, thiocyanates have low toxicity. The ammonium salt has an LD_{50} of 500 mg/kg for animals (van Hoek, 1995 ; see Table 4.3). The toxicity of thiosulphates is even lower and is about equal to that of common salt. Thiosulphates are extremely unstable, particularly at lower pH values and have a half life of only a few days in soils. Thiocyanates are also unstable in the environment. Their half-life in the environment has been assessed at about 6 months (Hung and Pavlostathis 1997). Provided that neither chemical can be leached quickly into ground-water systems, they are unlikely to present a serious environmental problem.

Table 4.2. Economics of phytomining for gold using root crops (tops+roots)

Plant or treatment	Gold yield (g/ha)*	Gold value ($US)	Final yield ($US)**
THIOCYANATE			
Carrot	779	7790	+840
Onion	162	1620	-5330
Red beet	75	750	-6200
Salad radish	237	2370	-4580
Oriental radish	209	2090	-4860
THIOSULPHATE			
Carrot	1450	14500	+7550
Onion	79	790	-6160
Red beet	47	470	-6480

*From final column of Table 4.1.

**After subtraction of $6950/ha for agronomic, incineration and chemical costs.

Table 4.3. Toxicity of various reagents including the three (asterisked) used in the leaching experiments

Name	Formula	Toxicity(LD_{50}) in mg/kg	Toxicity class
Sodium cyanide	NaCN	2.3	1
Ammonium thiocyanate*	NH_4SCN	500	3
Sodium thiocyanate	NaSCN	764	4
Ammonium thiosulphate*	$(NH_4)_2S_2O_3$	2500	4
Sodium sulphate	Na_2SO_4	4470	5
Water (uncontaminated)	H_2O	None	None

Source: Merck catalogue (1999)

4.6 Conclusion

This study has shown that root crops such as carrot may have potential for phytomining for gold provided that climatic and other conditions are suitable for this root crop. Further tests will of course be necessary to establish the potential of various carrot cultivars for phytomining. It would also be interesting to investigate the possibility of using tropical and subtropical plants and root crops such as wild cassava, sorghum (a canelike tropical grass cultivated for fodder and its sugary sap) and sweet potato to extend the scope of phytomining to warmer parts of the globe where these crops are often present and where local people have experience in their cultivation. It is true that there are additional costs involved in harvesting root crops, but this is more than offset by the much higher gold yield of the below-ground plant parts.

CHAPTER 5 - INDUCED UPTAKE OF GOLD AND MERCURY BY PLANTS FOR THE PURPOSE OF PHYTOEXTRACTION

5.1 Introduction

Metal contamination of soils is associated with, among other things, mining and smelting of ores, recycling of scrap metals, and poor industrial waste disposal. Remediation of contaminated soil requires special technical expertise because of the various forms of metals brought about by changes in soil environmental conditions. Furthermore, cleaning contaminated soils is very costly as it requires sophisticated equipment and land to transfer the contaminants to.

Phytoextraction is used to describe two types of operations, phytomining and phytoremediation. Phytomining is the use of plants to mine metals for commercial gain. This may serve as an alternative mining method for areas which can not be exploited using conventional methods or where ore grade is too low to warrant further mineral processing e.g. mine tailings. Phytoremediation is the *in situ* removal or improvement of soils contaminated by toxic metals by using plants.

Plants to be used for phytoextraction usually need to have the special characteristics of being hyperaccumulators. While all plants have the ability to remove metals from the soils, hyperaccumulators have 100 times the elemental concentration of "normal" vegetation growing in the same environment (in the case of gold 1 mg/kg Anderson *et al.*, 1998). Hyperaccumulation can be induced by addition of chelating agents such as thiocyanate, thiosulphate and thiourea to the substrate so as to make the targeted metals soluble.

Utilisation of plants to remove metals from soils has been demonstrated in the greenhouse and laboratory but only a few practical applications of phytoremediation have been undertaken so far. Different plants (*Brassica juncea,* chicory, *Berkheya*

coddii, *Linum usitassimum* and lucerne) were grown in Tui mine tailings amended with different amounts of lime. The possibility of using these crops for phytoextraction of gold and mercury was determined by separately adding the chelating agents ammonium thiocyanate and thiourea at rates of 1 g/kg and ammonium thiosulphate at a rate of 2 g/kg to the substrate after a growth period of 9 weeks. The plants were harvested 10 days later and analysed for gold and mercury by GFAAS and/or flameless atomic absorption spectrometry (see Chapter 2). Gold and mercury concentrations were higher in *B. juncea* and chicory than in the other plants. From the limited data obtained, it was difficult to conclude that plants could be used to extract gold economically. However, the two plants proved to be viable for use in the remediation of mercury. It was concluded that, gold and mercury uptake by *Brassica juncea* was positively correlated using ammonium thiosulphate.

5.1.1 Artisanal miners and the use of mercury

The biggest cause of mercury contamination in poor countries is the result of unregulated mining activities by poor artisanal gold miners. Virtually all countries in the world where gold or gemstones are mined, have artisanal mining activities. Apart from a very small proportion of traditionally mined gold, all gold mining has potentially heavy environmental costs, as it usually involves the use of either cyanide or mercury. Artisanal mining is a very ill-defined terminology. Having been involved with artisanal miners, by way of offering technical advice on the geology and safe mining and processing methods in Tanzania, I prefer to define it as a low-cost mining method where someone uses simple rudimentary skills to achieve a certain objective without applying expensive conventional technical methods. Some prefer to define it as "a simple way of encompassing all small, medium, large, informal, legal and illegal miners who use rudimentary processes to extract gold from secondary and primary ore bodies" (Veiga 1997). In gold mining, artisanal miners use a simple informal unregulated technology that relies on the formation of a gold-mercury amalgam to recover gold. Due to the inefficiency of the whole process, poor handling of mercury, ignorance of the hazards and the "get rich quick" attitude in most gold boom areas, plus

the fact that most of these areas are in the tropics where temperatures are above 20^0C almost throughout the year, mercury is saturated in the air and freely inhaled or mishandled by the users or spilled on the ground and eventually pollutes the environment. An artisanal miner works on instinct, and the need for feeding his family and getting his bills paid are to him a primary consideration. The health or safety issues are secondary. The concept of survival is constantly the driving force for these individuals.

Clearly, miners and their communities are at immediate risk. The UK-based Ecologist magazine cited a study conducted in the Philippines which showed that of people exposed to mercury for an average of 30 months, or who lived within 500 metres of a source of mercury, almost 75% of those examined showed clinical symptoms of poisoning. And tests from several mining communities in Brazil found that more than 30% of miners examined had mercury levels above the World Health Organization's tolerable limit (Moody, 1996).

Artisanal mining is a labour-intensive occupation, which involves both men and women. In many countries it has its own taboos and discipline. In almost every country, women are not allowed to go in underground mines. At least one out of six miners is a woman, involved mainly in cooking for the miners, some chores and social activities. In the 1980's in South America alone, over 1 million people were involved in artisanal mining producing over 190 tonnes of gold emitting over 200 tonnes of mercury annually to the environment. In countries where gold mining is the dominant mineral activity, the trend is the same (see Table 5.1). In Tanzania, there were over 100,000 people involved in artisanal gold mining in the 1980s, producing a conservative figure of 2.5 tonnes of gold annually. There are no proper production records because most of the gold is illegally smuggled out of the country. On the basis of production trends in South America, Tanzania would have produced around 20 tonnes of gold from artisanal mining, emitting roughly 20tonnes of mercury. It is estimated that artisanal miners produce up to 20% of Africa's gold. In the sub-Sahara

region, more than 1.5 million people work in the informal mining sector, while in Zimbabwe the figure is also put at 100,000 (Moody, 1996)

Table 5.1. Estimated gold production and number of miners involved in South America and Tanzania.

Country	Gold production (tonnes) p/a	Number of miners
Brazil	30-50	200,000-400,000
Colombia	20-30	100,000-200,000
Peru	20-30	100,000-200,000
Ecuador	10-20	50,000-80,000
Venezuela	10-15	30,000-40,000
Surinam	5-10	15,000-30,000
Bolivia	5-7	10,000-20,000
Mexico	4-5	10,000-15,000
Chile	3-5	6,000-10,000
French Guyana	2-4	5,000-10,000
Guyana	3-4	6,000-10,000
Nicaragua	1-2	3,000-6,000
Dominican Republic	0.5-1	2,000-3,000
Others	2-5	6,000-15,000
Total	115.5-188	543,000-1,039,000
Tanzania	15-20	80,000-100,000

Source: Veiga (1997).
Hester, B.W (1998)

Mercury is used in artisanal gold mining as the preferred amalgamation method because it is cheap. One kg of mercury can produce almost an equivalent weight of gold costing only $US 10 when it is used correctly (Veiga 1997). Mercury is poured over either sluice boxes or over crushed ore in a pan to amalgamate the metal, Some time the whole ore is spread on the ground and mercury poured over it, thus resulting in mercury losses, which are 3 times the amount of gold recovered. When gravity concentrates are amalgamated, the mineral portion is separated from the amalgam by

panning, forming an amalgamation tailing which is usually dumped into a water stream creating a "hot spot." Panning takes place either in water boxes or in pools excavated in the ground or at creek margins.

Mercury is an efficient reagent that can extract more than 90% of gold from gravity concentrates if used efficiently. Whether they labour in the rainforests of Amazonia or the banks of Tanzania's rivers, artisanal gold miners carry out a practice handed down from classical times to separate the gold from the earth. Excess mercury from the amalgamation step is removed by squeezing it through a material (such as a sisal sack or cotton cloth) by hand. Due to the inefficient way of separating the mercury from other metals, the amalgam usually remains with a 40% mercury excess which is extracted by centrifuging. Miners who prefer producing almost pure gold, destroy the other metals by roasting the metals in concentrated nitric acid in open pans or in retorts. The mercury burns off as a white vapour and is inhaled by the miners as they crowd around weighing up their shiny payroll. Some miners use the retort method, but this method is not very popular because the miners suspect being cheated as the retorts are usually covered. However, in research conducted by Dr. Mutagwaba of the State Mining Corporation Tanzania, and witnessed by myself, a transparent glass retort was developed which was acceptable to the miners. Research conducted in Canada found that losses of mercury to the atmosphere when retorts are not used are 50% as compared to 0.05% when retorts are used (Veiga 1997). Use of retorts should be encouraged as it tremendously reduces the amount of mercury discharged into the atmosphere where mercury is refluxed and recycled.

5.1.7 Mercury and gold

Mercury has a geochemistry similar to gold and the platinum group metals and is commonly associated with gold in practically all types of hypogene gold deposits. It is more often in small amounts (< 1 ppm) in the gold ore in the near surface veins. Mercury as cinnabar or in the form of secondary minerals is present in some gold

placers. In oxidised ores mercury is present mainly as remnant cinnabar and minor amounts of the native metal (Boyle, 1979).

5.1.8 Gold, mercury and plants

From their general geochemical similarities, plants could be induced to take up the two metals (mercury and gold). Induced phytoextraction could remove both mercury and gold from a contaminated environment. The key target metal for the operation would be mercury. However, this will depend on a proper chelate suitable to the two metals and type of plant which can remove both metals.

Gold extraction in economical amounts would be an added advantage and definitely a more viable proposition because it would help reduce the remediation costs. This chapter provides in part a preliminary overview of the remediation methods of decontamination by use of some plants to remove mercury from the soil and at the same time harvest gold that will have been taken up by the same plants. It also proposes a field trial model which could be adopted for phytoextraction in artisanal gold mines (particularly Tanzania).

5.2 Aim of the experiment

The aim of the experiment described in this chapter was:

(i) to find out the possibility of using different plants for concomitant phytomining of gold and phytoremediation for mercury.

(ii) to find out the possibility of using a single plant for phytoextraction of mercury and gold.

5.3 Materials and Methods

5.3.1 Plants used

Plants selected for the experiments were *Brassica juncea, Berkheya coddii,* lucerne, chicory and *Linum.* Initially, seeds of the five plants were sown in standard commercial seed raising compost and later transplanted into a Tui tailings substrate.

5.3.2 Tui mine tailings substrate

After at least the first pair of true leaves had appeared, plants were grown in finely sieved (<2 mm) Tui tailings and an equal volume of pumice sieved to<2 mm. "Osmocote" slow-release fertiliser was added to the substrate at the rate recommended by the manufacturer. The gold concentration in the Tui tailings ranged from 0.5 to 1.0 mg/kg (ppm). The mercury concentration was determined as 2.1 mg/kg.

5.3.3 Design for plant growth experiments

Plants in varying replicates for each of the four treatments (controls, thiocyanate, thiosulphate and thiourea) were grown for 9 weeks in 250 mL or 500 mL plastic pots. Out of the 107 plants, 67 (*Linum*, chicory, and *B. juncea*) were treated with different rates of lime (i.e 8 controls, 15 plants 0% lime, 14 plants 0.02% lime, 15 plants 0.04% lime, and 15 plants 0.06% lime).The remaining 40 plants were not amended with lime. The temperature in the greenhouse was maintained between 20-25^{0}C with random changing of pot positions to ensure consistency of illumination. At the end of the growing period, thiocyanate and thiourea were applied as a solution at a rate of 1 g/kg of substrate and ammonium thiosulphate was added to the substrate as a solution at the rate of 2 g/kg of substrate. After a period of 10 days, the thiocyanate-treated plants had died, although those treated with thiosulphate and thiourea still had viability. The plant

material was then harvested, washed thoroughly with RO water and dried at 70^0C. The dried plant material was separated (shoots and roots) and weighed.

5.4. Chemical analysis

5.4.1 Analysis of gold in plant samples

After weighing and packing the samples in borosilicate flasks, 10 mL of concentrated HNO_3 was added to each flask which was heated over a hotplate until the volume was reduced to almost dryness. Then 10 mL of concentrated HCl was added in the residue and heated over a hotplate until the volume had been reduced to about 1 mL. Finally, the residues were diluted to 10 mL with RO water and 5 mL was set aside for mercury determination, while 5 mL were analysed for gold as described in detail in chapter 2.

5.4.2 Determination of mercury in plant samples

The 5 mL aliquots were analysed separately for mercury using flameless atomic absorption spectrometry (see Chapter 2 for details).

5.5 Results and Discussion

A summary of results for total gold and mercury uptake by plants is shown in Figures 5.1 and 5.2.

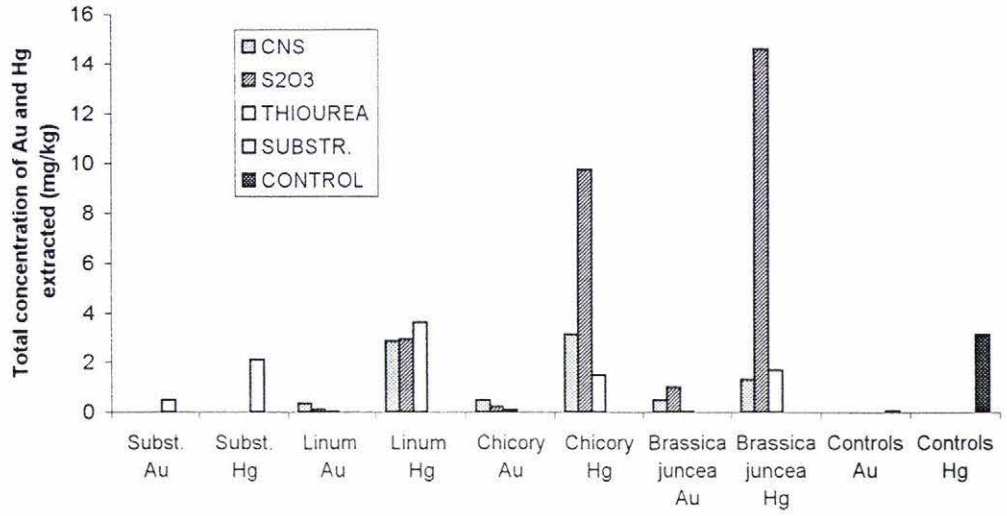


Figure 5.1. Gold and mercury uptake by plants grown in Tui mine tailings (0.06% lime) and treated with 2 g/L CNS, S_2O_3 and thiourea

5.5.1 Gold and mercury uptake by different plants by use of a substrate amended with lime

Induced uptake of gold by plants with addition of up to 0.06% lime

Use of ammonium thiocyanate:

After treatment with thiocyanate, the uptake concentrations of gold in both *Brassica juncea* and chicory was each 0.5 mg/kg while the concentration of gold in *Linum* was only 0.37 mg/kg. There was no significant uptake of gold in any of the control samples (see Figure 5.1).

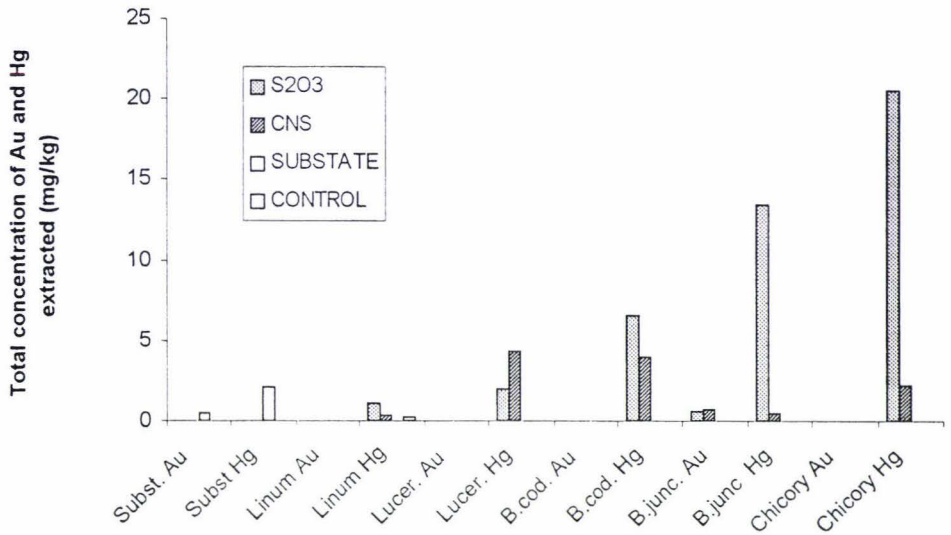


Figure 5.2. Gold and mercury uptake by plants grown in Tui mine tailings (no lime) and treated with 2 g/L CNS and S_2O_3. Control treatments showed metal uptake below the limit of detection.

Use of ammonium thiosulphate:

After treatment with thiosulphate, the uptake concentration of gold in *Brassica juncea* was just over 1 mg/kg (see Figure 5.1). This was obtained at a pH range of 6.7-7.3. Anderson (2000) proposed that at this pH range, gold would be soluble in thiosulphate and would be potentially available for uptake. The higher uptake concentration for thiosulphate treatment at this pH relative to thiocyanate treatment supports this theory. This shows that at higher pH, thiosulphate is more effective in mobilising gold than thiocyanate.

Use of thiourea:

Thiourea treatment of the substrate did not result in significant gold uptake for any of the plant species used (Figure 5.1).

Induced uptake of mercury by plants with addition of up to 0.06% lime

Use of thiocyanate:

After treatment with thiocyanate at a lime amendment of 0.04% the mercury concentration in chicory was 3.13 mg/kg, while the mercury concentration in *Linum* and *Brassica juncea* was only 2.85 and 1.32 mg/kg respectively. However, the chicory plants used as a control had concentrations of mercury of 3.1 mg/kg, which puts some doubts as to whether thiocyanate treatment on the substrate and using chicory does actually induce uptake (see Figure 5.1).

Use of thiourea:

The mercury concentration, after amendment with 0.02% lime and thiourea treatment in *Linum was* 3.7 mg/kg. Mercury concentration in *Brassica juncea* and chicory were only 1.7 and 1.5 mg/kg respectively (see Figure 5.1).

Use of ammonium thiosulphate:

The mercury concentration, after substrate amendment with lime of 0.02% and thiosulphate treatment in *Brassica juncea* was 14.6 mg/kg, and those of chicory and *Linum* were 9.75 and 2.92 mg/kg mercury respectively. Mercury concentration in the substrate was only 2.1 mg/kg while the chicory control showed some mercury concentration of 3.1 mg/kg. Of the three solutions used, it seems that thiosulphate is the best in inducing uptake of mercury. Furthermore, it seems that *Brassica juncea* and chicory are the only plants in this case that can be induced to uptake mercury (see Figure 5.1).

5.5.2 Gold and mercury uptake by plants using substrate not amended with lime

Results in Figure 5.2 show a summary of gold and mercury uptake by plants grown in substrates that were not amended with lime.. Note that without lime, five plants were used as compared to the above experiment where only three plants were used.

Induced uptake of gold by plants without lime addition

Use of thiocyanate:

For gold uptake, *Brassica juncea* proved to be superior to the other five plants used in the experiment. The gold concentration, after thiocyanate treatment, in *Brassica juncea* was 0.76 mg/kg while the other plants, chicory and *Linum*, gold concentrations were only 0.06 mg/kg 0.03 mg/kg respectively. *Berkheya coddii* and lucerne did not show detectable gold (see Figure 5.2).

Use of thiosulphate:

The gold concentration, after treatment with thiosulphate in *Brassica juncea* was 0.63 mg/kg while the concentration in the other spicies were below 0.04 mg/kg, below the substrate level of 0.5 mg/kg, but above controls which did not show any concentration of gold (see Figure 5.2).

Induced uptake of mercury by plants

Use of thiocyanate:

Of the five plants used for this experiment, lucerne showed the highest concentration of mercury compared with the rest. Lucerne showed a concentration of 4.35 mg/kg mercury while *Berkheya coddii*, chicory, *Brassica juncea* and *Linum* showed concentrations of 3.94, 2.28, 0.52 and 0.42 mg/kg mercury respectively (see Figure 5.2).

Use of ammonium thiosulphate:

Chicory showed the highest concentration of mercury in this experiment (20.47 mg/kg) *Brassica juncea* also showed a high concentration of 13.49 mg/kg mercury although this was similar to the results obtained previously of 14.57 mg/kg mercury when lime was added. The other plants also showed significant concentrations. *Berkheya coddii* showed 6.54, mg/kg lucerne showed 1.96 mg/kg mercury while *Linum* showed 1.11 mg/kg mercury. This may emphasise the use of thiosulphate as the most suitable reagent for mercury phytoremediation.

5.5.3 Correlation of gold and mercury

The degree of correlation of plant gold and mercury concentration varied between each species. In *Brassica juncea* the two metals showed some positive correlation (R^2= 0.22 see Figure 5.3). No correlation was apparent for chicory.

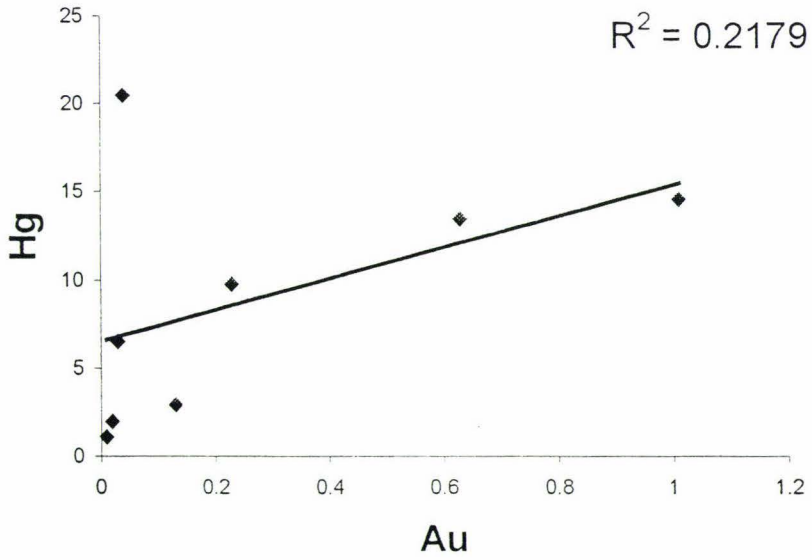


Figure 5.3. Regression of mercury vs gold in *Brassica juncea*. The correlation coefficient was 0.47 (P>0.10) and not significant.

5.6 The potential for phytoextraction of mercury and gold together in a single crop

5.6.1 Economic factors

The feasibility of a gold phytomining and mercury phytoremediation operation using induced hyperaccumulation has been examined, using a *Brassica juncea* crop with a biomass of 10 t/ha per annum and mercury concentration of 15 mg/kg:

15 mg/kg Hg in 10 tonnes of biomass	=	150 g/ha Hg
1.0 mg/kg Au in 10 tonnes of biomass	=	10 g Au worth US$100
1 ha of treated soil weighs 2000 t to depth 15 cm		
at 0.5g/kg S_2O_3	=	1,000,000 g S_2O_3
	=	1,000kg/ha
At US$1.50 of S_2O_3 per kg	= US$1,500/ha for removal of 150g of Hg	
Add capital costs ploughing	=	35
Cultivation	=	35
Drilling	=	20
Seed	=	65
Spraying	=	12
Fertilisers appl	=	15
Fertilisers harv	=	45
Spraying	=	30
Harvesting	=	70
Total cost	= US$1827	
Less value of a crop of gold	=	100
Net cost of removal of 150 g Hg	= US$1727 (loss)	

The cost of removal of 150 g of mercury can be reduced or changed to a small profit if the plants used for that purpose can hyperaccumulate gold to a higher concentration than the *Brassica juncea* used for the above model. Using carrots (see Chapter 4)

which have a high biomass yield of 16 t/ha dry weight and a metal concentration of above 50 mg/kg gold, and also on the basis of other researchers on carrots (see Table 1.2 which shows carrot roots having higher mercury content than the other vegetables 86 ppb), it could be possible to get a crop of gold valued at US$8000 (i.e 16x50) see Economic model Figure 5.4. It is important to note that in this experiment carrots were not used for phytoextraction for both mercury and gold.

Thus: Total cost = US$1827

Less value of a crop of gold = US$8000*

Net cost of removal of 150 g Hg = US$6173/ha (profit without offsetting costs)

*The figure does not take into account the cost of getting gold from plants. Assuming that 50% of the value of crop of gold will be used to offset such costs, then the profit will be reduced and the Economic model will look like:

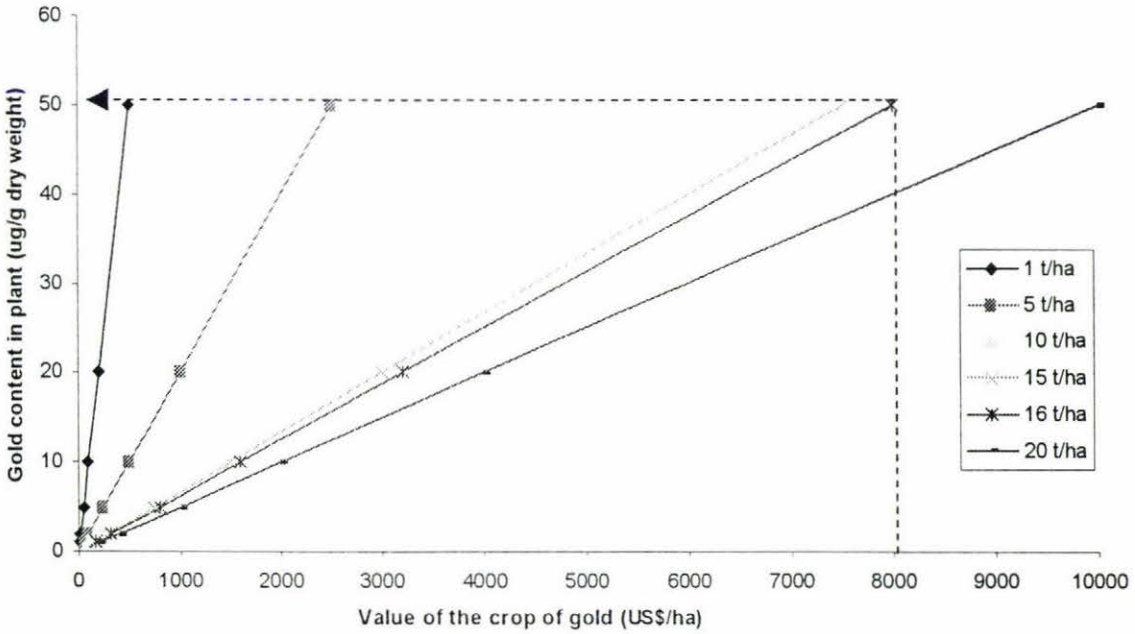


Figure 5.4. The value of a crop of gold for varying biomass values and for different gold concentrations in the dry plant material. These values are calculated for a gold price of US$284/oz or US$10/g. The value of a crop of gold using carrot plants of 16 t/ha biomass and gold concentration os 50 mg/kg is shown by the dotted line cutting the x-axis at US$8000.

Total cost	= US$1827
Less 50% of a crop of gold	= US$4000
Net cost of removal of 150 g of Hg	= US$2173 /ha (profit)

These values are of course a best-case scenario based on data from controlled laboratory experiments. In practice, the likely yield might only be a quarter of US$8000 but still representing a small profit. In any case, the scheme does not have to make a profit as its main aim is phytoremediation of mercury.

5.6.2 Practical application of phytoextraction to artisanal gold mining in Tanzania

Tanzania lies along latitudes 1^0 S to $11^0$45'S and along longitudes $29^0$21'E to $40^0$29'E on the African Plate which is one of the Earth's largest continental crusts. Tanzania's present geological form is a result of a series of events which began with evolution of the ancient Archaean Craton shield over 2.5 billion years ago.

The Tanzania Craton is one of the highly mineralised cratons in eastern Africa and is broadly similar to the cratons of Zambia, Zimbabwe and Kaapval (South Africa). Mineral deposits tend to occur in groupings which reflect the coincidence of factors favouring their formation. The grouping of mineral deposits is fairly distributed, the principal minerals being gold, diamonds, gemstones, coal, industrial minerals and base metals. The diamond grouping deposits include diamond-bearing kimberlites in the central part of the Tanzanian Craton. The gold deposits are mainly hosted by Archean greenstones and the banded iron formation of the Lake Victorian goldfields, metamorphic rocks of Proterozoic of Mpanda and the Proterozoic granitic and gneissic rocks of Lupa. Other economic mineral assemblage like nickel occur as pentlandite associated with chalcopyrite and pyrrhotite in the form of either massive or matrix sulphide bodies (Hester 1998).

The earliest organised prospecting and mining in Tanzania took place during the German colonial period. Gold discoveries began in the Lake Victoria region in 1894. Mining began at Sekenke Mine in 1909. After 1930, gold production was substantial (above 5 tonnes per annum) and increased steadily until after the Second World War. By 1967, the gold industry had declined but increased after 1975 when the world gold price increased greatly. Currently, the production is mostly from artisanal mining (above 2.5 tonnes per annum) and it is expected to pick up steadily after the changes made to the mining policy which has enabled many private companies (Anglo Americans, Ashanti gold, Cluff Minerals Sutton Resources etc) to peg claims in Tanzania (Hester 1998).

Small miners have for many years been operating in Tanzania, though not on the scale of countries in South America and some parts of Africa and Asia. While in other countries the artisanal miners have been receiving support of some kind from their governments, in Tanzania they have been regarded as illegal miners because of the crude methods employed in the trade (see Plate 5.1). However, of late, the government of Tanzania has organised a series of miners' cooperatives to facilitate purchase of equipment and sale of minerals, principally gold and gemstones. The government has been involved in educating the miners in the safe-handling of chemicals, especially mercury, and the move has had some positive results which have enabled the government to realise 2.5 tonnes of gold per year, which would have otherwise been sold illegally. Artisanal mining is conservatively estimated to employ over 100,000 people out of whom around 20,000 are women. Misuse and abuse of mercury, mainly due to ignorance of the hazards, is very common. It is probably important to mention here that, in practice, smelting and final processing of gold is more often than not done secretly in an enclosure where there is no enough ventilation, thus increasing the risks of inhalation of mercury vapour.

According to report published by Moody (1996) "Contamination of mercury occurs through the consumption of fish, and this is perhaps a greater long-term hazard. The constant flow of water used in the production process causes mercury to be washed into

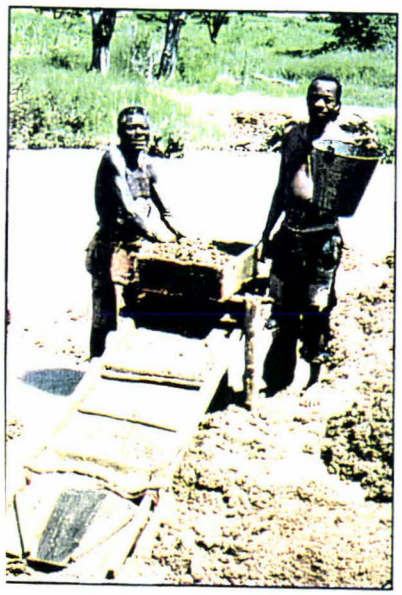


Plate 5.1 **Artisanal mining in Tanzania**

(clockwise from top left, Glory Hole, Prospect 30 Geita, crushing gold bearing rocks by wooden pestle and mortar, artisanal miners washing gold, artisanal miners recovering gold by panning). All photographs from special publication Opportunities for Mineral Development by (B.Hester 1998)

rivers. In a highly unregulated and competitive industry, many miners work ceaselessly to maximise earnings and take risks. Just how much spills is difficult to say. In Brazil, researchers say that for every tonne of gold produced, about one tonne of mercury is lost in spillage. In Brazil, tests on the Kayapo, whose territory is dotted by gold-mining excavations, indicate that 25% have high levels of mercury. The amount of mercury in the blood of children was found to be only slightly less than that in miners' blood."

Some of the mercury hazards are insidious and sometime mild cases of mercury poisoning can be overlooked for some other diseases like malaria and typhoid. Symptoms are often psycho-pathological which may result into incorrect diagnosis and when noticed the victims may be too poor to afford proper treatment. In some cases the harm may have advanced to a certain stage that they are considered as irreversible. It is not too late to think of "affordable" alternatives like growing plants which may possibly clean up the environment especially mercury and other metals in general.

It would be of great advantage to the government of Tanzania and in countries where artisanal mining is practiced, to run some field trials on how to clean contaminated soils using plants such as chicory and *Brassica juncea* (see Plate 4.2) and possibly carrots. I have a strong belief that plants such as wild cassava and some tropical yams (believed to hyperaccumulate cyanide) may be more appropriate in the tropics. These plants seem to have a high potential for phytoextraction, but more research on geochemistry of the soils involved and the type of plant for a particular soil and chelating solution need to be done for gold and mercury uptake.

Steps involved with phytoextraction for gold are summarised in a poster overleaf showing growing a crop of gold (Plate 5.2).

GROWING A CROP OF GOLD

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Step 1 - selection of a suitable site

- Many thousands of hectares of gold-bearing rock exist throughout Asia, the Americas, Africa and Australasia (Fig. 1).
- The gold content of this rock ranges from 0.1 to more than 2 g/ton, but is often unsuitable for conventional mining.

Figure 1 - mine tailings in Western Australia containing gold that may be suitable to plant uptake.

Step 2 - growing a crop of plants

- The selected area is seeded with a suitable plant species, or seedlings planted directly on site (Fig. 2).
- A suitable plant species is one that has a high biomass, rapid growth rate and is tolerant to extremes of salinity, aridity and heavy metal toxicity.

Figure 2 - a crop of the high biomass plant *Berkheya coddii*, native to South Africa.

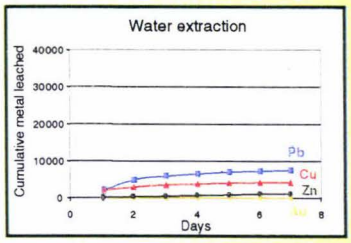

Figure 3a - column experiment where acid mine tailings was leached with water for 7 days (Cu, Zn and Pb x μg; Au - ng).

Step 3 - induced hyperaccumulation

- Once the crop has reached its maximum biomass, a chemical is applied to the site to make the gold soluble.
- Experiments at Massey University have used ammonium thiocyanate (SCN) and ammonium thiosulphate, both of which complex gold under different conditions.
- We have shown that ammonium thiocyanate is specific in solubilising gold (Fig. 3a,b).
- There is little risk of other dangerous heavy metals being leached into the groundwater.

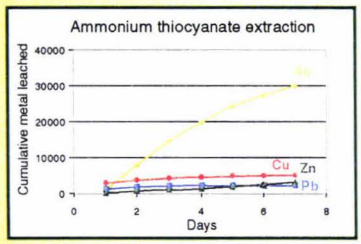

Figure 3b - column experiment where acid mine tailings was leached with SCN for 7 days (Cu, Zn and Pb x μg; Au - ng).

Step 4 - uptake

- Once the gold is soluble, plants act as a pump and hyperaccumulate gold inside living tissues (Fig. 4).
- All organs of a plant accumulate gold - roots, shoots and leaves.

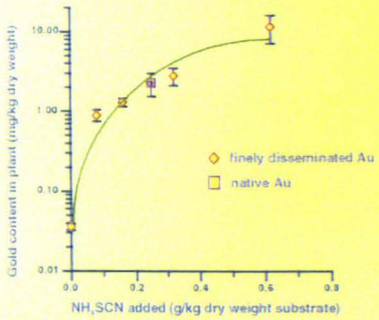

Figure 4 - induced uptake of Au by *Brassica juncea* from two types of artificial ore. After Anderson *et al.*, 1998.

Step 5 - harvesting and processing

- Eventually the crop will begin to die. This may take as little as a week, or as long as a month depending on the chemical used and concentration applied.
- At this point the biomass is collected and the gold processed (Fig. 5).

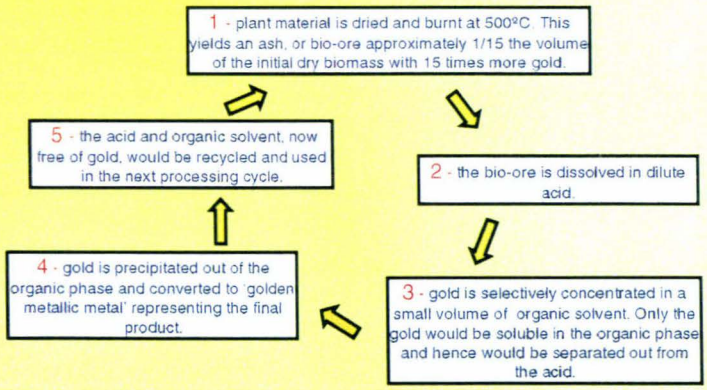

Figure 5 - a possible processing cycle for the recovery of gold from plants.

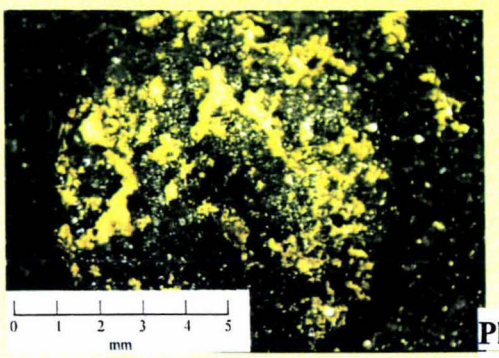

Figure 6 - the final product: gold recovered from plants.

Step 6 - the final product

- Figure 6 shows the amount of gold processed from 100 g of dried *Brassica juncea* plant material.
- There is only 0.7 mg of gold shown here, but when considered over a larger scale like a hectare, several hundred grams of gold could be recovered.
- Assuming not all the gold initially present at the site was removed in the operation, the cycle could continue, and the phytomining process repeated.

Reference Anderson C W N, Brooks R R, Stewart R B and Simcock R (1998) Harvesting a crop of gold in plants. *Nature* 395: 553-554.

Plate 5.2

A poster summarising the steps involved with phytoextraction For gold- Growing a Crop of Gold

5.6.3 Proposed model for field trials for gold and mercury phytoextraction in Tanzania

Before field trials on phytoextraction are undertaken, the project will require mineral policy backing. The objectives of the Mineral policy of the Government of Tanzania are:

- to stimulate exploration and mining activities;
- to regulate and improve artisanal mining;
- to ensure that wealth generated from mining support sustainable economic and social development; to minimise or eliminate the adverse social and environmental impact of mining activities;
- to promote and facilitate mineral and mineral based products' marketing arrangements;
- to alleviate poverty especially for artisanal and small scale miners;
- to promote and develop Tanzania as the gemstone centre of Africa (Ministry of Energy & Minerals, United Republic of Tanzania) Tanzania Mining – "A New Engine for Growth."

It will be seen from the mineral policy above that the project will have the backing of the government i.e. The Ministry of Energy and Minerals. So field work that is to be undertaken can be channelled through the government for direction and compliance.

The purpose of this project will be to put into practice what has been tried in the greenhouse and laboratory with regards to phytoextraction. Tanzania, as one of the countries involved in artisanal gold mining has been affected by mercury hazards and risks underlined earlier.

Areas with intermediate-stage prospects (artisanal activity or good value surface samples) Tanzania has many artisanal gold mining sites, among them are:

- Buziba, in the Rwamagaza greenstone belt (see Plates 5.3 and 5.4).
- Rwamagaza, in the Rwamagaza greenstone belt.

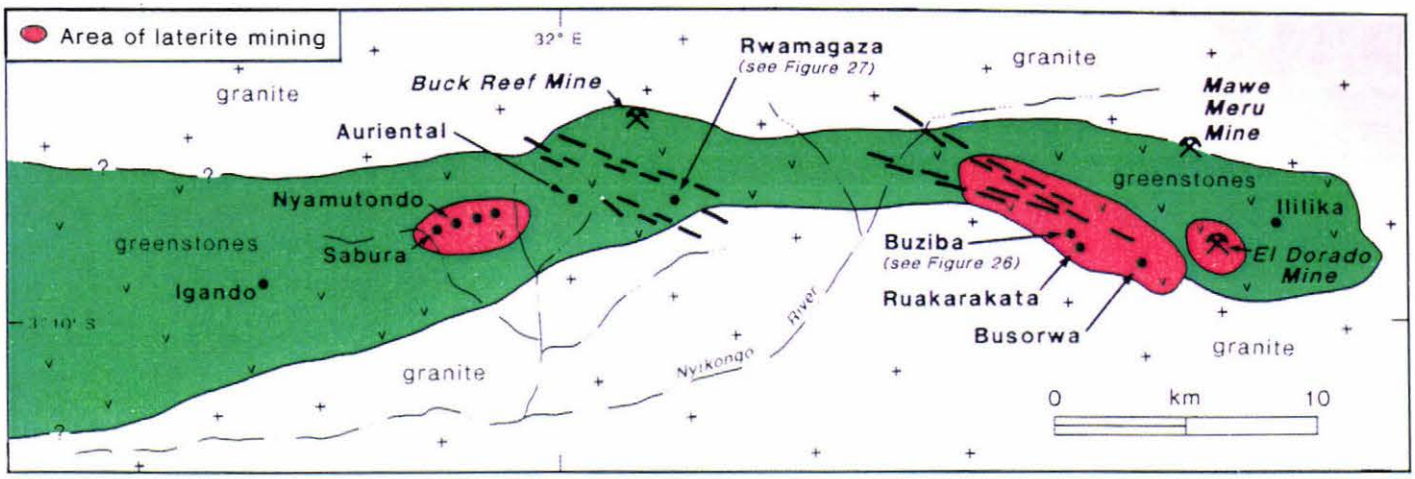

Plate 5.3 Area of laterite mining Rwamagaza greenstone belt Geita

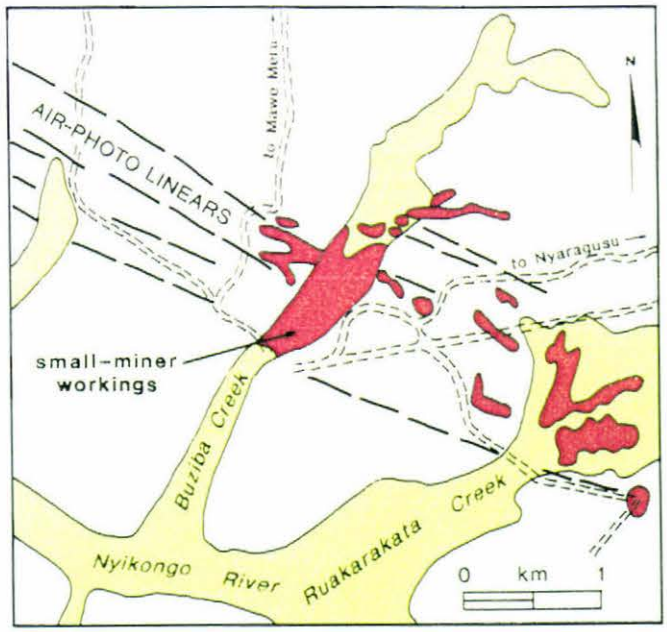

Plate 5.4 Geological map of Buziba Creek prospect in Rwamagaza Geita

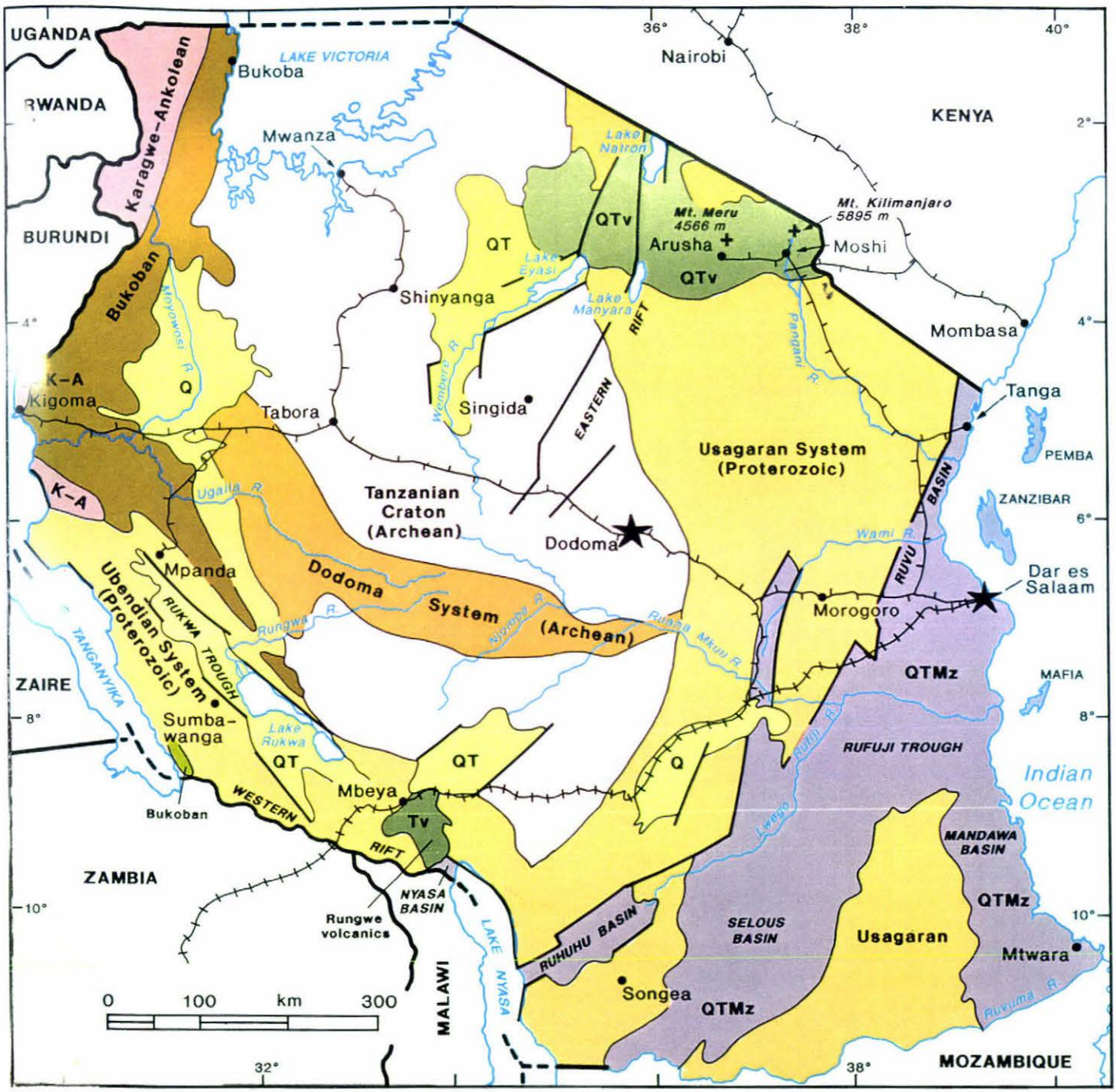

PLATE 5.5 GEOLOGICAL MAP OF TANZANIA

- Matinje Mine in the Nzega greenstone belt, where mineralised rubble zones overlie higher-grade quartz veins.
- Kitowero, in Proterozoic rocks of the Masasi High (southeast Tanzania) where metamorphosed greenstones and a banded iron formation may be the source of gold placers.
- Mbinga, in Proterozoic rocks of south-west Tanzania, a scene of intense artisanal activity.

The chosen site for this proposed project is Buziba Creek in Rwamagaza greenstone belt (South West of Lake Victoria). This site would be chosen because of its long history of high artisanal gold mining activity. According to my experience of the area and that of Hester (1998), "Several small deposits of tailings are known which might be of interest to a small scale producer. Sampling of dumps indicates extraction of gold at the larger mines was very effective. Little recoverable gold remains." The creek was very famous for washing, gold amalgamation and smelting.

Brief Geology of the Buziba creek

The Buziba creek is at the Eastern end of the Rwamagaza greenstone belt; it has a strong correlation between the area of alluvial gold deposits being worked by artisanal miners and linear features visible on area photographs as seen in Plates 5.3 and 5.4. These linear features coincide with magnetic surveys detectable from the ground. The high magnetic responses obtained over these linear features is probably due to the presence of ultramafic rocks as seen in some of the samples from underground artisanal prospecting pits (Hester, 1998).

Almost the whole area of what is called the Lake Victoria Zone (over 200 km around the lake) which comprises eastern, southern and south-western area of Lake Victoria, hosts the gold deposit in the Archean greenstone belt (Rwamagaza and Buziba included) and the banded iron formation. All rivers and tributaries flow into the lake which acts like a big water catchment for the whole gold region. This is the area where

90% of Tanzania's gold is produced i.e the vicinity of Lake Victoria (see Plate 5.5 Hester, 1998).

Materials and Methods for the proposed field trial

After intense sampling to determine areas with high mercury contamination, high gold concentration, pH of the substrate and the geochemistry of the soil, a $13x12m^2$ area in the creek preferably a "hot spot"(area where amalgamation tailings are dumped) would be cleared and levelled. At the same time seeds of different plant species such as chicory, *Brassica juncea*, salad radish, salad orient and carrot, would be sown in standard commercial seed raising compost. I propose the use of these plants because of the encouraging results shown in the laboratory and the greenhouse in experiments conducted by myself and other researchers. Another plant, cassava, would be grown in one of the project sites as a trial. Wild cassava has a history of hyperaccumulation of cyanide and a characteristic large biomass. Cassava is also a fast growing native plant which can withstand extreme temperature, water stress, acidity and salinity variations.

The area would be subdivided into thirty 2x2m plots. There is a half or one metre of open space between the plots depending on the treatment to allow access (see Figure 5.5). Apart from the cassava plot, which may accommodate at most 5 plants, the other plots may accommodate roughly 169 plants placed 15 cm. apart.

Prior to seeding or planting, the area to be mined would first be amended to attain the appropriate geochemical conditions that will be optimal for phytoextraction and plant growth. Once the plants have attained the maximum biomass, the area would be irrigated with the appropriate solubilising chemical to induce hyperaccumulation. Two chemicals namely ammonium thiocyanate and ammonium thiosulphate are to be chosen for this project. Calcium carbonate (lime) would be chosen to raise the pH in areas where the soils were acidic. In saline soils aluminium sulphate would be chosen. The amount of sulphur or lime will depend on the pH levels of the soil (see Table 5.2) The table below gives a rough guide with application to New Zealand soil (Manawatu Silt Loam). The optimal pH for plant growth varies between plant species (Appendix

2). Once metal and/or chemical stress in the crop inhibits transpiration (metal uptake occurs during transpiration), the plants would be harvested, the biomass incinerated and the metal recovered.

Thiosulphate treatment				**Thiocyanate treatment**				**Controls**
Chicory Without lime	O	Chicory with lime	O	Chicory without lime	O	Chicory with lime	O	Chicory
Carrot Without lime	P	Carrot with lime	P	Carrot without lime	P	Carrot with lime	P	Carrot
Brassica juncea without lime	E	*Brassica juncea* with lime	E	*Brassica Juncea* without lime	E	*Brassica juncea* with lime	E	*Brassica Juncea*
Salad radish Without lime	N	Salad radish with lime	N	Salad radish without lime	N	Salad radish with lime	N	Salad radish
Wild cassava Without lime		Wild cassava with lime		Wild cassava without lime		Wild cassava with lime		Wild cassava
Oriental radish without lime		Oriental radish with lime		Oriental radish Without lime		Oriental radish With lime		Oriental radish

Figure 5.5. Schematic field plan of proposed artisanal gold mining experiment in Tanzania

Physical and Chemical Analysis

Incineration of plants will be done in the site. However, chemical analyses could be conducted at Eastern Africa Mineral Resource Development Centre (EAMRDC) laboratory in Dar es Salaam or at the Ministry of Minerals Laboratory in Dodoma. If all

these places prove to be unqualified for analyses, the samples would be analysed at Massey University (Department of Soil and Earth Science, New Zealand).

Table 5.2. A rough guide to pH soil amendment

Initial pH	To lower pH to 5.0 add Elemental Sulphur at rate of	To raise pH to 6.5 Add Lime at rate of
6.1)		
6.0)	135g/m^2	110gm^2
5.9)		
5.8)	120g/m^2	170g/m^2
5.7)		
5.6)	90g/m^2	220g/m^2
5.5)		
5.4)	65g/m^2	330g/m^2
5.3)		
5.2)	35g/m^2	440g/m^2
5.1)		
5.0)		550g/m^2

Source: Massey University Department of Soil Science Levin Horticultural Field Days (1986)

Successful conclusion of this envisaged field trial would allow realisation of the practical application of a mercury/gold phytoextraction operation in artisanal areas of Tanzania.

5.7 Conclusions

From the data at hand it can be concluded that chicory and *Brassica juncea* could be used for phytoextraction of gold and mercury. Without addition of lime, (i.e under acidic environment) thiocyanate treatment induced uptake of gold by *B. juncea* and the

uptake of mercury by chicory. The addition of lime (i.e under alkaline environment) promotes uptake of gold and mercury by *B. juncea* using thiosulphate.

Positive correlation of gold and mercury shown by *B. juncea,* places this plant in a better position than the other plants to be used in field trials. Furthermore, the use of thiosulphate as a complexing agent seems to be favourable compared to thiocyanate and thiourea for inducing *B. juncea* to uptake both gold and mercury and chicory to uptake mercury. Thiosulphate has other advantages in that it is less expensive and less toxic than the other chemicals.

In the economic model derived from using a biomass of 10 t/ha for phytoremediation of mercury, the project would make a loss of US$1727 based on the gold concentration of 1 mg/kg. If other plants such as carrots are used which had concentrations of gold much higher than 50 mg/kg (see Chapter 4) the project could be made profitable. A return of US$2173/ha to remove 205 g/ha of mercury is conceivable.

The economic model in this research showed the value of a crop of gold for varying biomass values and for different gold concentrations in the dry plant material. These values were calculated for a world gold price of US$284per oz. or US$10 per g. The model showed the importance of high concentration of metals in the tissues with high biomass in plants. As a way of an example, a biomass of say 10 t/ha at a concentration of 5 g/t of gold would yield 50 g/ha Au. Using a biomass of 5 t/ha at a raised concentration of 10 g/t of gold would give an equal yield of 50 g/ha. The later would be more profitable because the lower biomass will mean less associated power costs for incineration of plant material.

In any case, when considering phytoremediation, phytomining is taken as secondary while phytoremediation is taken as primary. Any gold recovered would pay some of costs of the operation. It would be easy to convince the local communities on such a project because it is environmentally friendly and at the same time they raise value (gold) in return.

CHAPTER 6 – GENERAL CONCLUSION

The following summary of conclusions can be drawn from the results of the experiments:

6.1. General

1. Ammonium thiocyanate appears to be highly selective for removal of gold when acid mine tailings are used as a substrate. Thiocyanate is a prime solubilising agent for gold in phytomining operations. However, this solubilising agent is pH dependent. It is most effective at low pH.

2. At low pH, leaching of base metals is a function of pH, not complexation with thiocyanate. The results of Chapter 3 show that thiocyanate did not increase the solubility of base metals, relative to water, from mine tailings that were not amended with lime. However, leaching of gold clearly occurs through the formation of a soluble-metal complex with thiocyanate.

3. Root crops such as carrot could have high potential for phytomining for gold provided that climatic and other conditions are suitable for this root crop. Further tests are necessary to establish the potential of various carrot cultivars for phytomining. Accumulation of gold appears higher in the roots of some plants than in the shoots.

4. Both chicory and *Brassica juncea* could be used for the phytoextraction of mercury from acid mine tailings, as shown by experiments conducted on the Tui mine tailings. However, *Brassica juncea* is the only one that can significantly be used for phytoextraction for both mercury and gold. For this substrate unamended with lime (low pH) the use of ammonium thiocyanate or ammonium thiosulphate solution as a solubilising promoted metal uptake. However, with addition of lime (high pH) uptake

of gold and mercury by *Brassica juncea* was favoured by treatment with thiosulphate, while the addition of lime suppressed the uptake of both gold and mercury by chicory following treatment with thiosulphate.

5. Uptake of gold and mercury in experiments conducted for this thesis was maximised through the use of ammonium thiosulphate as a 'chemical inducing agent' and *Brassica juncea* as an 'induced hyperaccumulator' plant species. The practical ramifications of this are encouraging, as the use of thiosulphate as a complexing agent is favourable because of its lower cost and toxicity relative to thiocyanate and thiourea.

A general conclusion which can be derived from the above is that, before a particular plant and complexing agent is chosen, one has to have a good understanding of the geochemistry of the targeted soil. Tui tailings are well-weathered sulphide ores that could easily be leached by the solutions used. Water can even mobilise some of the metals in the Tui tailings such as zinc. In general the following principle holds true: For gold phytomining at low pH, use ammonium thiocyanate; but at high pH, use ammonium thiosulphate. The particular plant species to be employed would similarly be based on the geochemical conditions prevalent: a plant species that could grow in conditions that often pose an edaphic challenge.

6.2 Future outlook

The importance of living in harmony with the environment surrounding us cannot receive greater emphasis. Contamination of the soils with heavy metals (mercury) can be prevented, but once it happens, it would require costly equipment and expertise to remove the contaminants. Plants offer alternative methods of cleaning such soils. It is high time scientists develop practical and applicable procedures of using plants in the field that can help alleviate the problem of mercury in soils. However, more research work is needed especially with complexing agents which can induce solubility and therefore increase the uptake of gold and mercury by plants, and a better understanding of geochemistry of the soils in relationship to the applicable complexing agents. This

will allow the choice of plant species that will optimise modelled and physical uptake for a wide range of metals.

It would be appropriate to mention here that, most of the artisanal gold mine workings are in the tropics where temperatures and rainfall are high almost year-round. In which case mercury vapour is always in the atmosphere where artisanal gold mining is practiced. From my experience, educating the public about the hazards of mercury, and the use of retorts will alleviate the mercury hazards but will not remove mercury which is already in the soils. Should field trials prove fruitful, the use of plants will help to remove contaminants already in the soils, and I think it would be a good idea for different affected countries to implement a phytoextraction technology after that. However, I am not proposing here that phytoremediation measures will solve the problem now and forever, because with state of the current technology, it may take a few years of cropping before total remediation is achieved. To begin with, research can be conducted in the field as field trials in areas where contamination of heavy metals is extensive.

To reiterate what I have previously emphasised, a strong consideration of use of indigenous tropical plants such as wild cassava (believed to hyperaccumulate cyanide, and to be resistant to adverse weather conditions and toxic environments) could be given priority because it has an extensive root system. I have proposed a field trial model for phytoextraction in Tanzania that could form the basis for future challenges. I am very optimistic that the realisation of practical application of phytoextraction is in sight, and now is the right time it is put into practice.

With development in scientific knowledge in harnessing the environment and growing awareness of the dangers of mercury pollution and increasing vigilance of our environmental monitoring, one can look to the future with considerably more optimism than was possible a few years ago.

APPENDICES

Appendix 1. Detailed data on gold in plants experiment (oriental, radish, carrots, beetroots and onions.
Appendix 2. The pH requirements of various plants, vegetables and flowers.

Appendix 1 Detailed data on gold in plants experiment (oriental, radish, carrots. Beet roots and onions)

	plant.			in ppm	(Ax10)	
1A Y26/80	**RADISH**	Leaves	0.5204	0.684	6.8	13.1
1B Y27	**in CNS**	Roots	0.3797	3.301	33	86.9
2AY28	"	Leaves	0.2833	0.012	0.1	0.42
2BY29	"	Roots	0.2896	3.641	36.4	125.7
3AY30	"	Leaves	0.253	0.892	0.9	3.51
3BY31	"	Roots	0.1771	3.889	38.9	219.6
4AZ1	"	Leaves	0.7386	0.0229	0.23	0.3
4BZ2	"	Roots	0.9323	1.339	13.4	14.4
5AZ3	"	Leaves	0.2596	0.0231	0.23	0.9
5BZ4	"	Roots	0.3174	1.452	14.5	45.7
6AZ5	"	Leaves	0.1402	0.00848	0.1	0.6
6BZ6	"	Roots	0.0952	1.695	17	178
7AZ7	"	Leaves	0.3796	1.076	10.8	28.3
7BZ8	"	Roots	0.1582	4.832	48.3	305.4
8AZ9	"	Leaves	0.2206	0.443	4.4	20.1
8BZ10	"	Roots	0.1417	2.227	22.3	157.2
9AZ11	"	Leaves	0.4941	1.084	10.8	21.9
9BZ12	"	Roots	0.339	3.907	39.1	115.3
10AZ13	"	Leaves	0.117	0.282	2.8	24.1
10BZ14	"	Roots	0.1102	1.053	10.5	95.6
11AZ15	"	Leaves	0.3784	0.605	6.1	16
11BZ16	"	Roots	0.4763	0.0087	0.09	0.2
12AZ17	"	Leaves	0.2894	0.646	6.5	22.3
12BZ18	"	Roots	0.1457	1.884	18.8	129.3
13Z19	"	Leaves	0.1283	0.002	0.002	0.02
14AZ20	"	Leaves	0.2893	0.278	2.8	9.6
14BZ21/80	"	Roots	0.3171	3.909	39.1	123.3
15AZ22	"	Leaves	0.898	0.0117	0.12	0.1
15BZ23	"	Roots	0.2864	0.831	8.31	29
16AZ24	"	Leaves	0.661	0.297	3	4.5
16BZ25	"	Roots	0.8075	0.758	7.6	9.4
28AY22	"	Leaves	0.4504	0.392	3.9	8.7
28BY23	"	Roots	0.2813	1.943	19.43	69.1
17AZ26	**ORIENTAI**	Leaves	0.6332	0.713	7.1	11.2
17BZ27	**in CNS**	Roots	0.092	0	0	0
18AZ28	"	Leaves	1.1155	0.105	1.1	0.9
18BZ29	"	Roots	0.2916	0.493	4.9	16.9
19AY41/80	"	Leaves	1.2226	0.019	0.2	0.2
19BY6	"	Roots	0.5307	1.222	12.2	23.1
20AY71/80	"	Leaves	1.264	0.283	0.2	0.1
20BY8	"	Roots	0.4678	1.248	12.5	26.7
21Y9	"	Leaves	0.2219	0.539	5.4	24.3
22AY10	"	Leaves	1.0137	0.827	8.2	8.2
22BY11	"	Roots	0.1481	2.397	24	161.9
23AY12	"	Leaves	0.9275	1.024	10.2	11
23BY13	"	Roots	0.1528	3.617	36.2	236.7
24AY14	"	Leaves	1.0492	0.172	0.1	0.1
24BY15	"	Roots	0.4415	2.929	29.3	66.3
25AY16	"	Leaves	0.8067	0.071	0.7	0.9
25BY17	"	Roots	0.3088	1.444	14.4	46.8
26AY18	"	Leaves	0.6657	0.627	6.3	9.4

26BY19	"	Roots	0.2472	0.506	5.1	20.5
27AY20	"	Leaves	0.63	0.903	9	14.3
27BY21	"	Roots	0.2257	7.24	72.4	320.8
CONROL CARROTS		(no chemicals added)		"A"	Ax10	Ax10/Wt.
1A	0.7846	Leaves	Total Wt.	0.042	0.42	0.54
1B	0.6999	Roots	1.4845	0.107	1.07	1.53
2A	0.4605	Roots		0.028	0.28	0.6
2B	1.188	Leaves	3.37	0.184	1.84	1.35
3A	0.4704	Leaves		0.116	1.16	3.53
3B	0.5307	Roots	1.0011	0.064	0.64	1.21
CONTR0L BEETROC		T(no chemicals added)				
4A	0.3971	Leaves		0.043	0.43	1.08
4B	0.3608	Roots	0.7579	0.024	0.24	0.67
5A	0.6877	Leaves		0	0	0
5B	0.416	Roots	1.1039	0.032	0.32	0.77
6A	0.4024	Leaves		0.17	1.7	4.22
6B	0.2304	Roots	0.6328	0	0	0
CONTROL ONION		(no chemicals added)				
7A	0.0659	Leaves		0	0	0
7B	1.3076	Roots	1.3735	0	0	0
8A	0.3128	Leaves		0	0	0
8B	0.4606	Roots	0.7734	0	0	0
9A	0.1317	Leaves		0	0	0
9B	0.412	Roots	0.5437	0	0	0
TREATED WITH CNS		CARROTS				
10A	0.2622	Leaves		0.082	0.82	3.12
10B	0.077	Roots	0.3392	0.625	6.25	81.2
11A	0.6291	Leaves		0.202	2.02	3.21
11B	0.3597	Roots	0.9888	0.55	5.5	15.3
		ONIONS				
12A	0.1781	Leaves		0.01	0.1	0.56
12B	0.1804	Roots	0.3585	0.443	4.43	24.6
13A	0.1043	Leaves		0.284	2.84	27.23
13B	0.348	Roots	0.4523	0.483	4.83	13.9
14A	0.1381	Leaves		0.115	1.15	8.33
14B	0.5945	Roots	0.7326	0.165	1.65	2.78
		BEETROOTS				
15A	0.9971	Leaves		0.339	3.39	3.39
15B	0.3323	Roots	1.3294	0.301	3.01	9.05
16A	1.084	Leaves		0.528	5.28	4.87
16B	0.4778	Roots	1.5622	0.097	0.97	2.03
17A	0.7505	Leaves		0.562	5.62	7.49
17B	0.5533	Roots	1.3048	0.425	4.25	7.68
18A	0.294	Leaves		0.303	3.03	10.31
18B	0.1788	Roots	0.4728	0.022	0.22	1.23
TRATED WITH S2O3		ONIONS				
19A	0.1606	Leaves		0.146	1.46	9.09
19B	1.1286	Roots	1.2892	0.033	0.33	0.29
20A	0.1281	Leaves		0.251	2.51	19.6
20B	0.3734	Roots	0.4015	0.123	1.23	3.29
21A	0.2457	Leaves		0.879	8.79	35.8
21B	0.4617	Roots	0.7074	0.199	1.99	4.31
		BEETROOTS				
22A	0.3015	Leaves		0.152	1.52	5.04
22B	0.0743	Roots	0.3768	0.022	0.22	2.96

23A	0.5545	Leaves		0.12	1.2	2.16
23B	0.3735	Roots	0.928	0.144	1.44	3.85
24A	0.7684	Leaves		0.275	2.75	3.57
24B	0.5564	Roots	1.3248	0.174	1.74	3.12
25A	0.7532	Leaves		0.337	3.37	4.47
25B	0.3705	Roots	1.1237	0.175	1.75	4.72
26A	0.8049	Leaves		0.292	2.92	3.62
26B	0.4385	Roots	1.2434	0.074	0.74	1.68
27A	0.6637	Leaves		0.378	3.78	5.69
27B	0.2953	Roots	0.959	0.088	0.88	2.98
		CARROTS				
28A	0.7865	Leaves		1.142	11.42	14.5
28B	0.1272	Roots	0.9137	2.41	24.1	189.5
29A	0.2471	Leaves		0.225	2.25	9.1
29B	0.3102	Roots	0.5573	2.751	27.51	88.7
30A	0.4638	Leaves		0.737	7.37	15.9
30B	0.629	Roots	1.0928	0.672	6.72	10.7
31A	0.9233	Leaves		1.117	11.17	12.1
31B	0.3322	Roots	1.2555	2.251	22.51	67.8

Appendix 2 The pH requirements of various plants, vegetables and flowers.

Crop Name	(Vegetable Garden)	pH range
Asparagus		6.0 - 6.8
Beans (Broad)		5.5 - 6.8
Beans (Snap)		5.5 - 6.8
Silver Beet		6.0 - 6.8
Red Beet		6.0 - 6.8
Brassicas		6.0 - 6.8
Carrots		5.5 - 6.8
Celery		6.0 - 6.8
Cucumber		5.5 - 6.8
Kumara		5.5 - 6.8
Leeks		6.0 - 6.8
Lettuce		6.0 - 6.8
Onions		6.0 - 6.8
Parsnips		6.0 - 6.8
Peas		5.5 - 6.8
Potatoes		5.0 - 6.8
Pumpkins		5.0 - 6.8
Rhubarb		5.0 - 6.8
Spinach		6.0 - 6.8
Sweetcorn		5.5 - 6.8
Tomatoes		5.5 - 6.8
Turnips		5.5 - 6.8
	(Flower Garden)	
Anemones		7.5 - 8.0
Azalea		4.5 - 5.5
Blueberry		4.5 - 5.5
Boronia		4.5 - 5.5
Camellia		4.5 - 5.5
Carnation		6.2 - 6.8
Chrysanthenum		6.2 - 7.4
Daphne		4.5 - 5.5
Delphinium		6.2 - 6.8
Ericas		4.5 - 5.5
Eucalypts		4.5 - 5.5
Lilies		6.0 - 7.0
Rhododendron		4.5 - 7.0
Roses		5.5 - 7.0
Zinnia		6.2 - 6.8

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